RUBBER CHEMISTRY

AND TECHNOLOGY

Guanidines as Accelerators and Activators

The guanidines (DPG and DOTG) have been available since 1920 for use as accelerators. Their use as a primary accelerator has been largely replaced by the thiazoles since the early 1930's. However, their use as secondary accelerators has accounted for their continued growth. As a result of their basicity, guanidines have a strong activating effect on the thiazoles. This accounts for their extensive use as secondary accelerators particularly in butadiene-styrene copolymers which cure at a slower rate than natural rubber. They still find use as primary accelerators, especially in highly loaded mechanical stocks. The relative characteristics of DPG and DOTG as both primary and secondary accelerators are best illustrated by the examples given below.

Using natural rubber and a loading of 90 to 100 parts of filler, normal amounts of oils, stearic acid, antioxidants and 2.5 parts sulfur, the following characteristics can be obtained:

	1.0 part DOTG	1.43 parts DPG
Mooney Scorch @ 240°F	11 min.	7 min.
Rex Hardness at Full Cure	64	64
Mod. @ 300% (Optimum Cure)	550 psi	550 psi
Tensile (Optimum Cure)	3000 psi	3025 psi

The use of DOTG gives a safer processing stock.

The results of oven aging and oxygen bomb aging indicate that the DPG accelerated stock exhibits somewhat better aging characteristics than the DOTG accelerated stock.

DPG and DOTG, used as activators for MBTS in this same high loaded base formula, gave the following results:

	0.6 part MBTS 0.2 part DOTG	0.6 part MBTS 0.3 part DPG
Mooney Scorch @ 250°F	24 min.	17 min.
Rex Hardness at Full Cure	65	64
Mod. @ 300% (Optimum Cure)	500 psi	525 psi
Tensile (Optimum Cure)	3050 psi	3125 psi

The aging characteristics of the activated thiazole accelerated stocks are considerably better than those for the straight guanidine accelerated stock. Again, the DPG activated stock has somewhat superior aging characteristics to the DOTG activated stock.

In a cold butadiene-styrene copolymer stock with 50 parts HAF black and 2 parts sulfur, DPG and DOTG were used as secondary accelerators with the following results:

	0.8 part MBTS 0.25 part DOTG	0.8 part MBTS 0.25 part DPG
Mooney Scorch @ 262°F	24	21
Mooney Scorch @ 280°F	12	11
Rex Hardness at Full Cure	71	70
Mod. @ 300% (Optimum Cure)	2050 psi	2150 psi
Tensile (Optimum Cure)	3550 psi	3475 psi

The scorch characteristics indicate that DOTG gives somewhat more processing safety than DPG when used as an activator for thiazoles. The modulus figures indicate a slight curing strength advantage for DPG.

* * *

More complete data on the above illustrations, and many others, is contained in the recently issued Cyanamid Technical Bulletin No. 848, *The Guanidine Accelerators*. If you are interested in these products, we, or the Cyanamid representative in your area, will be glad to supply a copy of this bulletin to you.

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THE AMERICAN CHEMICAL SOCIETY

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Office of Permanent Historian....H. L. TRUMBULL

71ST MEETING OF THE DIVISION OF RUBBER CHEMISTRY HELD JOINTLY WITH RUBBER CHEMISTRY DIVISION OF CHEMICAL INSTITUTE OF CANADA, SHERATON-MT. ROYAL HOTEL, MONTREAL, MAY 15, 16, 17, 1957

This meeting was the first one held jointly by the Division of Rubber Chemistry of the American Chemical Society and the Chemical Institute of Canada. It was well attended as shown by the following breakdown of registration:

ACS Members	791
CIC Members	110
Non-Members	216
Ladies	199
Total	1,316

The 25 year club with Dr. Norman S. Grace as chairman held its 18th meeting on May 15. Approximately 300 members were present at lunch. The honor for having the longest service to the rubber industry went to a guest, Mr. C. B. Copeman, publisher of the *Rubber Journal of London* and official representative of I.R.I. Mr. Copeman's length of service was 51 years.

Highlights of this dinner program were the greetings and comments from The Honorable Herve L'Heureux, U. S. Consul General at Montreal and from Mr. C. S. Richardson representing the Canadian government.

The main feature of the program was the presentation of the Colwyn Medal, awarded by the Institute of Rubber Industry, London, to Mr. William B. Wiegand for his work in the field of carbon blacks. A comprehensive history of Mr. Wiegand and his accomplishments was ably given by Dr. Whitby.

After the Medal presentation, Chairman Garvey thanked the Local Arrangements Committee and Mr. Huggenberger for the excellent meeting and program. He then turned the proceedings over to the Entertainment Chairman. An excellent variety show was provided.

Chairman Garvey opened the business meeting by calling for a minute of silence in memory of those members who have passed on since the previous meeting:

Arthur M. Neal
Harmon Connell
Ernest B. Caldwell
Roger A. Mathes
L. F. Rogers

Dr. Garvey spoke feelingly about the very considerable contributions of Dr. Neal as Secretary of the Division and to the rubber industry. His passing represents a great loss.

Chairman reported appointments made by the Executive Committee of S. D. Gehman, an Associate Editor, *R. C. & T.*, S. G. Byam, Acting Secretary and R. H. Gerke, Secretary for the balance of year.

Dr. Garvey also reported on plans being made to strengthen the Division organization. These are:

1. A manual "The Duties and Functions of Officers, Directors and Various Committees", prepared by J. M. Ball and S. G. Byam and submitted to the Executive Committee.
2. Appointment of assistants for the Secretary, Treasurer and Advertising Manager of *R. C. & T.* These appointments will be considered later this year.
3. Extension of the term of office for Secretary and Treasurer from 1 to 3 years. An amendment to the By-Laws to implement this will be proposed at the fall meeting.

The membership of the Division was reported as being 2544 members, 509 associates, for a total of 3,053.

Chairman Garvey announced that the Charles Goodyear Medal Committee had selected Arthur W. Carpenter as the Medalist for 1957. The presentation of the Goodyear Lecture and of the Medal will take place at the fall meeting.

The Nominating Committee, composed of D. F. Behney, Chairman, H. G. Bimmerman, M. L. Freeman, H. H. Osterhof and R. A. Emmett, presented the following slate to be voted on this summer and to serve in 1958.

Chairman	R. F. Dunbrook, Firestone Tire & Rubber Co.
Vice-Chairman	E. H. Krismann, du Pont Co.
	S. C. Nicol, Goodyear Tire & Rubber Co.
Secretary	R. H. Gerke, U. S. Rubber Co.
Treasurer	G. E. Popp, Phillips Chemical Co.

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Northern California	R. J. Reynolds, Shell Development Co.
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	K. C. Tregillus, Vernay Labs.
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	M. A. Youker, du Pont Co.
Connecticut	W. C. Carter, Pequanoc Rubber Co.
	H. Gordon, Bond Rubber Corp
Detroit	R. W. Malcolmson, du Pont Co.
	J. F. Stiff, Columbian Carbon Co.
Rhode Island	R. B. Robitaille, Phillips Chemical Co.
	R. W. Szulik, Acushnet Process Co.
Washington, D. C.	G. W. Flanagan, B. F. Goodrich Chemical Co.
	A. W. Sloan, Atlantic Research Corp.

All registrants, including the ladies, were entertained delightfully at the Mountain Chalet, top of Mt. Royal by the City of Montreal with excellent food and beverages. Greetings were extended by Acting Mayor Murray Hayes, followed by a gracious acknowledgment and appreciation by Chairman Garvey. This reception was a highlight of the meeting.

TECHNICAL PROGRAM

B. S. GARVEY, JR., Presiding

1. Opening Remarks, Chairman B. S. Garvey, Jr.
2. "The Application of Near-Infrared Spectroscopy to the Analysis of Polymeric Materials. I. The Identification of Polymers and Polymer Mixtures", by M. J. BROCK and GEORGE D. LOUTH, Chemical & Physical Research Laboratories Firestone Tire & Rubber Co., Akron, Ohio
3. "The Application of Near-Infrared Spectroscopy to the Analysis of Polymeric Materials. II. The Quantitative Absorptiometric Determination of Elastomers in Rubber Products", by K. E. KRESS, General Laboratory, Firestone Tire & Rubber Co., Akron, Ohio
4. "The Dunlop Rotary Resilience Machine", by D. BULGIN and G. D. HUBBARD, The Dunlop Research Centre, Birmingham. To be presented by A. D. DINGLE, Dunlop Research Centre, Toronto
5. "Temperature Effects on Elastomer Flow Patterns in the Mooney Viscometer", by DAVID CRAIG, A. E. JUVE, L. O. SCHROYER, C. E. SITZ, R. A. HARRINGTON, and ROSS SHEARER, B. F. Goodrich Co., Brecksville, Ohio
6. "An Electronically Instrumented Pendulum for Evaluating Impact Absorption of Foam Materials", by C. S. WILKINSON, JR., Research Division, Goodyear Tire & Rubber Co., Akron, Ohio
7. "A Constant Torque Abrader with a Permanent Abrasive Surface", by IRA WILLIAMS, J. M. Huber Corp., Borger, Texas

O. R. HUGGENBERGER, Presiding

8. "Lignin as a Reinforcement for GR-S in Military Pattern Tires," by LLOYD KRICHEW, Director of Vehicle Development, Dept. of National Defence, Ottawa, Ont., D. W. MACGREGOR, Howard Smith Paper Mills, Cornwall, Ont., and T. R. GRIFFITH, National Research Council, Ottawa
9. "A Study of the Moisture Adsorption Properties of Carbon Blacks", by Eli M. DANNENBERG and WEBSTER H. OPIE, JR, Godfrey L. Cabot, Inc., Boston, Mass.
10. "Infrared Studies of the Chemical Constitution of Carbon Black Surfaces", by HARVEY M. COLE and ELI M. DANNENBERG, Godfrey L. Cabot, Inc., Boston, Mass.
11. "Improving the Carbon-Rubber Bond", by H. A. BARENDLE, Columbian Carbon Company, New York
12. "Carbon Black," by W. B. WIEGAND-Colwyn Medal address

J. D. D'IANNI, Presiding

13. "The Thermal Diffusivity of Butyl Rubber and Its Compounds", by R. L. ZAPP and D. R. MACRAE*, Enjay Laboratories, Linden, N. J.

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* Present address, Graduate School, Princeton Univ., Princeton, N. J.

14. "Details on the Half Life of Polymeric Free Radicals", by G. Gold-finger et al., Armour Research Foundation (and the University of Buffalo), Chicago, Illinois

15. "The Dependence of Tack Strength on Molecular Properties", by W. G. Forbes and L. A. McLeod, Polymer Corp., Limited, Sarnia, Canada

16. "Electronically Sorted Punched Cards for Polymer Compounding Data", by R. F. Neu, Enjay Laboratories, Linden, N. J.

17. "The Coding of Rubber Properties into a Specification", by Glenn E. King, Yale Rubber Mfg. Co., Sandusky, Mich.

18. "Resorcinol-Formaldehyde Latex Adhesives for Bonding Synthetic Tire Cords", by Myron I. Dietrick, Petrolia Development Laboratory, Koppers Company, Inc., Petrolia, Pa.

19. "Radiation Effects in Elastomeric Vulcanizates", by B. L. Johnson, H. E. Adams, and Marie Barzan, Chemical & Physical Research Laboratories, The Firestone Tire & Rubber Co., Akron, Ohio

N. S. Grace, Presiding

20. "Vulcanizable Saturated Acrylate Elastomers", by Joshua Nelson, Fred Leonard, and George Brandes, Army Prosthetics Research Laboratory, Walter Reed Army Medical Center, Washington, D. C.

21. "Cure of Polyurethane Elastomers with Peroxides", by O. C. Keplin-ger and E. E. Gruber, General Tire & Rubber Company, Akron, Ohio

22. "The Cross-Linking of Butadiene-Acrylate Elastomers by Bases", by W. Cooper and T. B. Bird, Dunlop Research Centre, Birmingham. To be presented by R. T. Woodhams, Dunlop Research Center, Toronto.

23. "Control of Degradation in Oil-Extended Styrene-Butadiene Rubber", by R. J. Reynolds, Shell Development Co., Emeryville, Cal.

24. "Recent Developments in the Application of 'Kel-F' Elastomer", by Lester E. Robb, Francis J. Honn, and David R. Wolf, M. W. Kellogg Co., Jersey City, N. J.

25. "Properties of Fluorocarbon Elastomer 214", by J. C. Montermoso, A. F. Wilson, and C. B. Griffis, Quartermaster Research and Development Center, Natick, Mass.

FUTURE MEETINGS

	Meeting	City	Hotel	Date
1957	Fall	New York	Commodore	September 11–13
1958	Spring	Cincinnati	Netherlands Plaza	May 14–16
1958	Fall	Chicago	Sherman	September 10–12
1959	Spring	Los Angeles	Biltmore	May 12–15
1959	Fall	Washington*	Shoreham	November 9–13
1960	Spring	Buffalo	Statler	May 24–27
1960	Fall	New York	Commodore	September 13–16
1961	Spring	Louisville	Brown	May 16–19
1961	Fall	Chicago	Sherman	September 5–8
1962	Spring	Boston	Statler	May 15–18

* An international meeting jointly sponsored by the Division of Rubber Chemistry ACS, Committee D-11 of ASTM, and the Rubber and Plastics Division of ASME.

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1957

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Chairman: H. W. Catt (B. F. Goodrich Co., Akron). *Vice-Chairman:* Sheldon Nicol (Goodyear Tire and Rubber Co., Akron). *Secretary:* Milton H. Leonard (Columbian Carbon Co., Akron). *Treasurer:* George Popp (Phillips Chemical Company, Akron). Terms end June 30, 1958. Meetings in 1957: October 25; in 1958: January 24, April 11, and June 20.

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CHICAGO

Chairman: A. E. Laurence (Phillips Chemical Co., Elmhurst). *Vice-Chairman:* V. Labrecque (Victor Mfg. & Gasket Co., Chicago). *Secretary:* M. J. O'Connor (O'Connor & Co., Inc., Chicago). *Treasurer:* J. Groot (Dryden Rubber Div., Sheller Mfg. Corp., Chicago). Terms end August 30, 1957. Meetings in 1957: October 20, November 15, December 20; in 1958: January 31, March 14 and April 25.

CONNECTICUT

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Chairman: D. K. Bonn (U. S. Rubber Co., Washington, D. C.). *Vice-Chairman:* R. D. Stiehler (National Bureau of Standards, Washington, D. C.). *Secretary:* A. W. Sloan (812 N. Fairfax St., Alexandria, Va.). *Treasurer:* J. Royden Moore (Firestone Tire and Rubber Co., Washington, D. C.). Terms end October, 1957. Meetings in 1957; January 16, February 13, March 20, April 17, May 15.

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Formed 1956, Provisional to 1958

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DETROIT
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General Tire & Rubber Co.
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 Memphis 2, Tennessee

NEW BOOKS AND OTHER PUBLICATIONS

TRANSLATION OF AN ARTICLE ENTITLED "BUTADIENE AND ITS POLYMERIZATION," by K. Ziegler, E. Eimers, W. Hechelhammer, and H. Wilms.—A number of copies of this translation are in the Rubber Division Library, Akron University, Akron, Ohio, and may be had by writing to Mrs. Lillian Cook, Librarian. Several copies are available for loan to members of the Rubber Division only and others are for sale at twenty dollars each. Checks should be made payable to George Popp, Treasurer. The original article appeared in the *Annalen der Chemie*, Vol. 567, pages 43–91, 1950. There is a growing interest in rubbery diene polymers and this paper is of lasting interest. It is felt that the next best thing to publication in RUBBER CHEMISTRY AND TECHNOLOGY is to make the translation available through the library.

TENTATIVE ASTM RECOMMENDED PRACTICE FOR NOMENCLATURE FOR SYNTHETIC ELASTOMERS AND LATICES*. ASTM Designation: D 1418-56T. Issued, 1956. This Tentative Recommended Practice has been approved by the sponsoring committee and accepted by the Society in accordance with established procedures, for use pending adoption. Suggestions for revisions should be addressed to the Society at 1916 Race St., Philadelphia 3, Pa.

Scope.—1. (*a*) This recommended practice establishes a new system of general classification for the basic elastomeric as well as rigid and semirigid raw materials produced and used by the rubber industry. It provides a classification system for rubbers and other elastomers both in dry and latex form determined from the chemical composition of the polymer chain, and defines and codes the "R" or rubber family of elastomers by insertion of the name and abbreviation of the monomer or monomers used before the "R".

(*b*) The purpose of this recommended practice is to provide a standardization of terms for use in industry, commerce, and government and is not intended to conflict with but rather to act as a supplement to existing trade names and trademarks. In the case of the term "Government Rubber Styrene" abbreviated "GR-S," it is intended to replace this term and abbreviation since it is no longer applicable after the production facilities were sold to private industry.

Classes of Basic Raw Materials.—2. The basic elastomeric and rigid and semirigid plastic materials produced and used by the rubber industry shall be named and classified as follows:

Class I.—Elastomers:
    A. Vulcanizable:
        1. Diene rubbers.
        2. Non-diene rubbers.
    B. Nonvulcanizable and other elastomers.
Class II.—Hard Plastics.
Class III.—Reinforcing Resins.
Class IV.—Paint Vehicles.

NOTE.—Chlorinated rubbers and cyclized rubbers are considered as end products of the rubber industry instead of raw materials.

Elastomers and Rubbers.—3. Elastomers and rubbers both in dry and latex form, shall be classified and coded from the chemical composition of the polymer chain in the following manner:

M—Elastomers having a saturated chain of the polymethylene type.
N—Elastomers having nitrogen in the polymer chain.
O—Elastomers having oxygen in the polymer chain.
P—Elastomers having phosphorus in the polymer chain.
R—Rubbers or elastomers having an unsaturated carbon chain, for example, natural rubber and synthetic rubbers derived at least partly from diolefins.
T—Elastomers having sulfur in the polymer chain.
U—Elastomers having carbon, oxygen, and nitrogen in the polymer chain.

Family Designations.—4. The "R" family, both in dry and latex form, shall be defined by inserting the name of the monomer or monomers before the word "rubber" from which it was prepared (except for natural rubber). The letter immediately preceding the letter R shall signify the diolefin from which the rubber was prepared (except for natural rubber). Any letter or letters preceding this diolefin letter signifies the comonomer or comonomers. The following classification shall be used for members of the "R" family:

BR—Butadiene rubbers.
IR—Isoprene rubbers, synthetic.
CR—Chloroprene rubbers.
NR—Isoprene rubber, natural.
ABR—Acrylate-butadiene rubbers.
IIR—Isobutylene-isoprene rubbers.
NBR—Nitrile-butadiene rubbers.
NCR—Nitrile-chloroprene rubbers.
PBR—Pyridine-butadiene rubbers.
SBR—Styrene-butadiene rubbers.
SCR—Styrene-chloroprene rubbers.
SIR—Styrene-isoprene rubbers.

NOTE.—When designating latex or latexes, the terminology shall be, for example, "SBR latex" or "SBR latexes".

RUBBER CHEMICALS. J. van Alphen, Rubber Stichting, Delft, The Netherlands. Elsevier Publishing Co., Amsterdam, The Netherlands. Sole distributor for the United States and Canada, D. Van Nostrand Co., Inc., New York, N. Y.; for the British Commonwealth except Canada, Cleaver-Hume Press, Ltd., London, England; and for Germany, Berliner Union, G.m.b.H., Stuttgart, Germany. Cloth cover, 6 by 9 inches, 164 pages. Price, U.S.A., $5.—This book has been compiled in an attempt to meet the need of a simple guide to the extensive and rapidly growing field of rubber chemicals on a world-wide basis, according to the preface written by R. Houwink, former general director of Rubber Stichting. The manuscript was originally prepared by J. van Alphen, at the request of H. C. J. de Decker, director of research for internal use in the laboratories of Rubber Stichting. W. J. K. Schonlau and M. van den Temple and others at the Dutch rubber research institute assisted in the work.

The authors restricted themselves to accelerators, activators, antioxidants, blowing agents, peptizing agents, retarders, and vulcanizing agents, with emulsifying agents and carbon blacks also listed according to types. For the first

major groups the chemical names are given together with a brief description of each material and its properties. The trade names and the suppliers in the various countries complete the discussion for each material. The trade names for a given compound are listed in alphabetical order, and an alphabetical index provides a means to find those materials of which only the name is known.

Although this book is not a complete listing of all compounding ingredients used by the rubber industry, it should be of general value both in this country and abroad. Its usefulness in the United States, however, may be reduced by the large number of compounds listed that are available outside this country. For example, the total number of accelerators listed is about 155, of which half are available abroad. Also, the author's preoccupation with emulsifying agents, 432 of which are listed, may not be of great value to the rubber compounder in this country. [From the *Rubber World*.]

DUTIES AND FUNCTIONS OF OFFICERS, DIRECTORS AND VARIOUS COMMITTEES OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY. MAY 15, 1957. Prepared by John M. Ball and Seward G. Byam. A number of copies of this definitive report were distributed at the recent Montreal meeting of the Division. A copy is in the Rubber Division Library at Akron University.

REPORT OF THE MEETING OF THE CHARLES GOODYEAR MEDAL COMMITTEE

Balloting for the Goodyear Medal Award resulted in the nomination of Arthur W. Carpenter, retired (B. F. Goodrich Co.), who was contacted by committee chairman A. E. Juve. He accepted the nomination with great pleasure and was then declared elected the Charles Goodyear Medalist and Lecturer for 1957.

There was considerable discussion about the variability and in some cases incompleteness of the nominations as received from the several nominators. It was suggested by R. D. Stiehler that all nominations be required to conform to an exact standard and that any not conforming be omitted from consideration. The committee felt this plan should be developed and made clear to the membership when the call for candidates is published in the rubber journals. This matter is to be discussed further at the fall meeting.

CONDUCTIVE BLACKS FOR HIGHLY CONDUCTIVE RUBBER

M. H. POLLEY AND B. B. S. T. BOONSTRA

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A paper under this title appeared in RUBBER CHEMISTRY & TECHNOLOGY, Vol. 30, pages 170–179 (1957). A wrong drawing was used for Figure 6 on page 177. The correct Figure 6 is as follows:
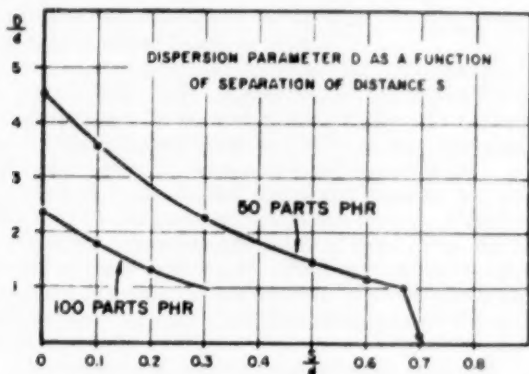
Also in line 14 from the bottom of page 170 "43 × 10⁷" should read 4.3×10^7.

RECENT DEVELOPMENTS IN HARDNESS TESTING *

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The purpose of this review is to outline the problem of standardization of the Shore Durometer Type A, report on the significance of a recent change made in the instrument, and to point out the relationship between the readings obtained on the revised Shore instrument and the International Organization for Standardization recently modified hardness scale.

Probably the most widely used physical test instrument in the rubber industry is the Shore Durometer. Approximately 15,000 of the Type A instrument (the quadrant type) have been made of which about 80 per cent are still in active use. Approximately 9000 of the Type A-2 (the round style) have been made, of which about 90 per cent are still in active use. A large percentage of these were sold in the United States and Canada, but substantial numbers have been sold throughout the rest of the world. Most rubber technologists have one in their possession and many of them carry one in their pockets during the course of their daily work. Testing laboratories employ them constantly, finished goods inspectors use them to check conformance with customer's specifications, and customers use them similarly to check incoming shipments of goods.

Because of carelessness in their use and the ease with which they could be damaged, it was found that these durometers often got out of calibration, so that some means of checking to a common basis was required. Twenty years ago, it was a common experience, in cross checks of the hardness of rubber compounds tested in different laboratories, to find differences between instruments as high as ten to fifteen units. This was an intolerable situation, since more and more consumers were specifying hardness limits on the products they were purchasing. It was essential that some common basis for standardization be developed.

The first serious attempt made to provide a procedure for standardization was by Larrick[1]. At the time of his report there was no ASTM method describing the characteristics of the instrument, although it was stated by Larrick that Committeee D-11 was at that time considering this instrument and several others with the view of establishing a method.

The first published reference to the specification for the Shore Durometer was by Shore[4] at a Symposium on Rubber in 1932. The specifications were stated to be: "This instrument . . . has been originally provided with a simple metric scale. It has a frustum cone impresser pin 3/64 inch in diameter, with the flat tip 1/32 inch. The pin begins to yield and the indicator hand departs from zero after a pre-pressure of 2 ounces, then proceeding up to 29 ounces at which point 100 is indicated on the dial. The total stroke of the pin is 0.1 inch so that each division on the dial would stand for 0.001 inch of depth travel which, while not regularly shown, would read inversely, that is, the zero for depth travel would be at 100 on the scale and 100 depth would be a zero of the adopted scale".

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* An original contribution.

Figure 1 shows the mechanism of the Type A Durometer. As the indentor is moved upward in the case, it causes the arm 7 to pivot about the point 8. The rack 9 rotates the pinion 10 and carries the pointer across the scale. The motion of the indentor into the case is resisted by the spring connected to the arm 7 through an adjustable linkage 4. The position of the lower end of this linkage may be moved laterally.
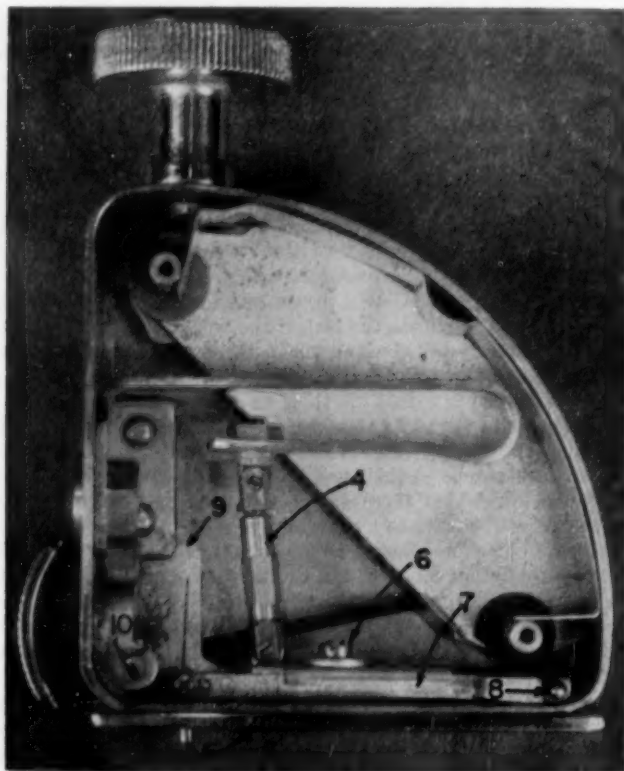
Fig. 1.

The motion of the pin relative to the case is indicated on the scale. The total possible motion is the distance which the pin extends beyond the case. At zero extension the pointer should indicate 100 on the scale and at its maximum extension the pointer should indicate zero. When the instrument is pressed against a rubber specimen, the forces exerted by the indented rubber and the spring in the instrument are balanced and some value between 0 and 100 will be indicated in the scale. For a particular rubber the value shown will depend on the load-deflection curve of the instrument, the pin extension, and the condition of the indentor.

Two adjustments permit modification of the load-deflection curve. These are the position of the slide 6 and the length of the linkage 4. These adjust-

ments can usually be made so that the load-deflection curve is a straight line showing a zero reading with 56 grams (2 ounces) applied to the indentor and a reading of 100 with 822 grams (29 ounces) applied.

The pin extension can have no effect on the load-deflection curve, but it does have an effect on the reading obtained.

It was stated by Shore as quoted above that the extension of the pin from the base plate should be 0.100 inch so that a movement of 0.001 inch corresponds to one unit on the hardness scale. In Larrick's report a table lists the measured pin extensions of five durometers whose specification indentor length is given as 0.09375 inch. There is no explanation of the source of this figure. However, it is of interest that four of the five durometers were close to this value; one however, was 0.101 inch.

The first issue of the ASTM Method D-676 was in 1942. In this version, the pin extension was specified at 0.092–0.095 inch which was apparently intended to bracket the above figure of 0.09375 inch. In 1947 the method was amended and the pin extension specified at $0.100 \pm .001$ inch. In 1949 it was again amended to specify a pin extension of $0.100 \; {}^{+\;.000}_{-\;.010}$ but a footnote suggested that manufacturers should attempt to adhere to the tolerances of $+ 000$ and $-.003$ inch. Actually, all durometers made during this period had pin extensions in the range of 0.092–0.095 inch.

The procedure recommended by Larrick[1] for standardizing Shore Durometers is as follows:

(1) The instrument is put into good mechnical condition, that is, cleaned, bearings set properly to minimize friction, pointer adjusted, parallax eliminated, and backlash in the rack and pinion reduced as far as feasible.

(2) The base of the pin is examined under a micrometer microscope. If not flat and circular the pin is either replaced or ground.

(3) The load-deflection curve is adjusted to a straight line; the pre-pressure is taken as 57 grams (2 ounces) and the 100 division load as 822 grams (29 ounces) on a 0.0312 ± 0.003 inch diameter indentor. If the diameter of the base is larger, or smaller, than 0.0312 inch the loads are changed in direct proportion. A tolerance of not more than 5 grams is permitted on the load at any point. (Tolerance permitted by present D-676-55T is 4 grams.)

(4) The length of the pin protruding from the rest plate is adjusted until, when the durometer is pressed against a flat plate glass surface, the pointer covers the 100-division mark on the scale.

(5) The final check on adjustments (3) and (4) is made with the back of the case closed tightly by means of both screws.

(6) During readings, the durometer is held with the rest plate F parallel to the surface of the sample and pressed slowly against the sample with just sufficient force to insure contact. The initial deflection is taken as the reading.

It will be noted that it is possible to have a durometer which, though it is properly calibrated with respect to the load-deflection curve and though its pin extension is adjusted properly to read 100 on a glass surface, will nevertheless not give the correct hardness reading. This can occur if the indentor point is worn or damaged or if the diameter of the tip of the indentor is greater or less than 0.0312 inch. Since many laboratories do not have adequate facilities for observing or correcting these difficulties, it has made the problem of being certain whether or not a durometer is in proper calibration a most difficult one.

In practice it has been found advantageous for a particular laboratory to maintain a carefully adjusted durometer as a standard which is used only for checking the calibration of adjusted instruments. For this purpose, a series of blocks of rubber of varying hardness are maintained so that the adjusted instrument can be checked against the "master" instrument. Each of the larger companies does this and a cross check of several of them a few years ago indicated quite good agreement between the "master" instruments.

Following are the data obtained at this time:

Mfgr. A			Mfgr. B	Mfgr. C	Mfgr. D
Spec.	A	39	38 (− 1.0)	39 (0)	38 (− 1.0)
	B	44	43.5(− 1.5)	45 (+ 1)	44 (0)
	C	49	48.5(− 0.5)	50.6(+ 1.6)	49.8(+ 0.8)
	D	54	54 (0)	56. (+ 2.0)	55 (+ 1.0)
Natural	E	61	60.5(− 0.5)	62.3(+ 1.3)	61.2(+ 0.2)
Rubber	F	67	65.5(− 1.5)	68.3(+ 1.3)	67.2(+ 0.2)
Stocks	G	75	74 (− 1.0)	75.6(+ 0.6)	75 (0)
	H	81	80 (− 1.0)	81.3(+ 0.3)	80.8(− 0.2)
	I	83	82 (− 1.0)	84 (+ 1.0)	83 (0)
Spec.	J	40	39.5(− 0.5)	41.3(+ 1.3)	39 (− 1.0)
	K	46	45.5(− 0.5)	48.3(+ 2.3)	45.2(− 0.8)
	L	52	51 (− 1.0)	53 (+ 1.0)	50.4(− 1.6)
SBR	M	58	56 (− 2.0)	60 (+ 2.0)	57.2(− 0.8)
Stocks	N	64	63 (− 1.0)	65.3(+ 1.3)	63.6(− 0.4)
	O	69	67 (− 2.0)	70 (+ 1.0)	68.2(− 0.8)
	P	74	73.5(− 0.5)	75.3(+ 1.3)	74 (0)
	Q	80	78.5(− 1.5)	81 (+ 1.0)	79.8(− 0.2)
	R	84	82 (− 2.0)	83.6(− 0.4)	82.6(− 1.4)
Av. differences from Mfgr. A			(− 1.0)	(+ 1.1)	(− 0.3)

As mentioned earlier all Type A durometers made up to fairly recently had pin extensions in the range of 0.092 inch to 0.095 inch. In May 1954 a series of durometers numbered from 16301 to 16350 were made with a pin extension of 0.100 inch, and starting in March 1955 with number 16901 all durometers have been made with pin extension of 0.100 inch. Since the pointer motion is controlled by the motion of the pin relative to the case, it was necessary for the manufacturer to either change the scale (i.e., expand it) or to change the dimensions of the pinion gear. The former course was followed and the scale length of the new instruments is longer than the old ones.

This change affects the readings obtained moderately as will be shown later, in the direction of higher readings.

RELATIONSHIP BETWEEN THE INTERNATIONAL HARDNESS SCALE AND SHORE A DUROMETER SCALE

For a number of years the committee on rubber of the International Organization for Standardization (Committee ISO/TC45) has been working on an international hardness scale and method of hardness measurement. A draft of the proposal of this committee has been published[2]. To a considerable extent, this proposal followed the 1950 British standard which in turn was influenced by the excellent work done by J. R. Scott and his colleagues at the RABRM. One of the features of both the British standard of 1950 and the ISO proposal was the incorporation in a dead weight method of testing of a

scale which like the Shore scale extends from 0 (very soft) to 100 (infinitely hard). The draft proposal states that "Readings in International Rubber Hardness Degrees are approximately the same as those of the Shore Durometer Type A".

An instrument which meets the requirements of the proposed ISO method is the Wallace Dead Weight tester built by The H. W. Wallace Ltd., Croydon, England. A check of the results obtained with four of these instruments in four different laboratories against four "standard" Shore Durometers Type A on identical samples showed the following results on a series of natural rubber stocks:

	Average Wallace dead weight hardness	Average Shore hardness	Difference
1	40.9	36.5	4.4
2	44	40.1	3.9
3	60	56.5	3.5
4	69.9	67.	2.9
5	81.7	79.3	2.4

This was too great a discrepancy to permit the two scales to be used interchangeably. On checking into the reasons for this discrepancy between the reported close agreement between the two scales and the actual poor agreement, it was found that it was due to the lack of agreement on what is the "correct" Shore scale. In the work done by the British directed toward a standard hardness scale and in its subsequent adoption by the ISO, it was assumed that a "correct" Shore A instrument was one which had a pin extension of 0.100 inch. This was a reasonable assumption based on Shore's original description of the instrument and the limits specified in the ASTM Method D-676, since 1947. However, as mentioned earlier, the instruments produced actually had pin extensions in the range of 0.092–0.095 inch (which are in the range of 0.090 to 0.100 inch as specified in D-676 since 1949) and the effective industry standards were based on the instruments available.

Because of the wide use of the Shore Durometer in this country for specification purposes, a change in the scale as large as shown in the above tabulation would be intolerable. Two changes have been made in the direction of bringing the two scales into agreement: one by the manufacturer of the Shore instruments, as mentioned earlier, which was to increase the pin extension to 0.100 inch $^{+.000}_{-.003}$ with a suitably adjusted scale; and the other by the ISO group to move their scale slightly in the direction of the Shore scale. These two changes bring the two scales into essential agreement when low creep stocks are tested, as will be shown later.

The extent of the modification of the ISO scale is shown in the following table kindly supplied by J. R. Scott:

Old	New	Old	New
30	28.0	70	70.1
35	33.1	75	75.3
40	38.3	80	80.5
45	43.5	85	85.7
50	48.8	90	90.7
55	54.1	95	95.6
60	59.5	100	100
65	64.8		

In the curves shown hereafter in which hardness in accordance with the new ISO scale is shown, the data were obtained on the Wallace Dead Weight tester with the original scale and the values corrected using the above table.

HARDNESS BY DEAD WEIGHT TESTING VS.
"INSTANTANEOUS" HARDNESS

The qualification in the previous section concerning low creep stocks introduces a complication into the picture which needs clarification.

With a dead weight instrument the extent of penetration of the indentor depends on the "hardness" of the material and also its creep characteristics.
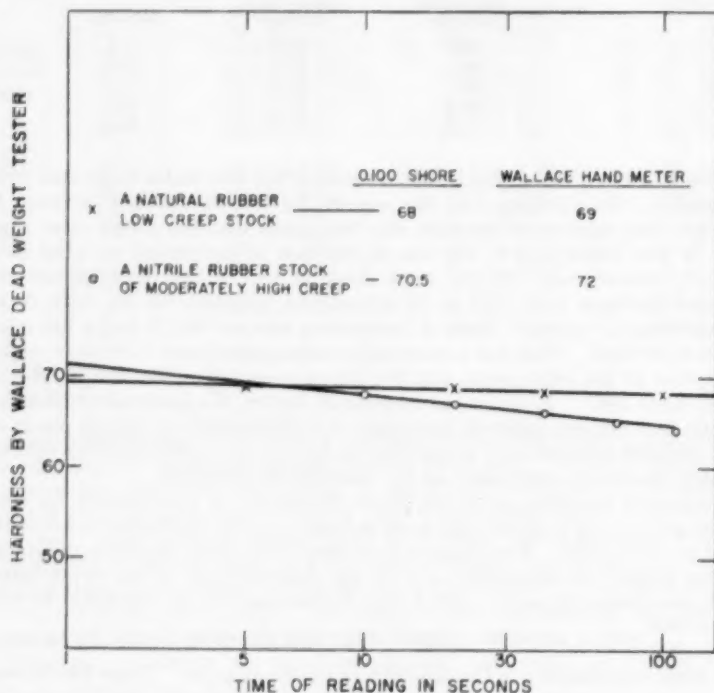
Fig. 2.

Because of mechanical difficulties, it is not practicable (with present, existing instruments) to apply the load on the indentor quickly and simultaneously to read the penetration.   Thus with all dead weight instruments, some fixed time such as 30 seconds or 60 seconds is prescribed at which the penetration is read. However, it is possible to make readings during the course of the test at various time intervals (about 5 seconds is the earliest practical time).   These values when plotted against log time give a straight line which may then be extrapolated to a shorter time, e.g., 1 second to give a value which will correlate reasonably well for high creep stocks with the "instantaneous" measurements obtained with an instrument such as the Shore.

To illustrate this point, two typical curves are shown in Figure 2, one for a low creep stock and one for a stock having moderately high creep, both of about the same hardness level. By the dead weight method at a 30 seconds reading time, the stock having the higher creep characteristics is rated softer than the stock with low creep (66.4 against 68.5), while by the 0.100 inch Shore and Wallace hand meter, they are rated in the reverse order.

What this means with respect to the relation between hardness measurements taken on a dead weight device meeting the requirements of the proposed ISO method and those obtained with a Shore A instrument is that for high
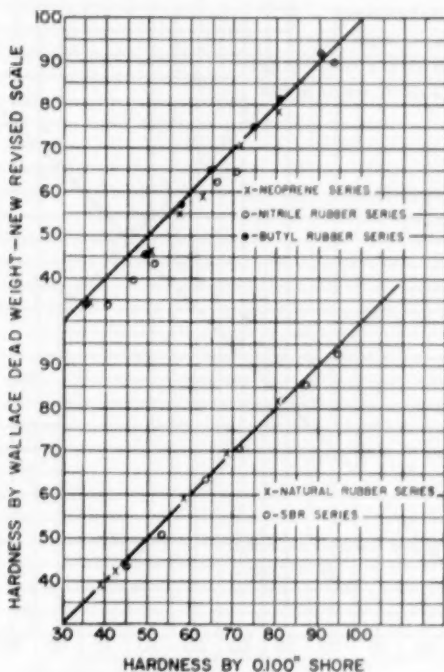
FIG. 3.

creep stocks the dead weight tester will give *low* values compared to the Shore A. The extent by which they will be low will vary depending on the creep characteristics of the stocks but may be as much as 8 to 10 units.

In further illustration of this point the curves in Figure 3 show first, the fact mentioned above that with good, low creep stocks the agreement between the 0.100 inch Shore and the latest modification of the ISO scale is very good. This is shown by the data for the natural rubber series. Second, they show a varying disagreement for stocks with higher creep properties amounting to as much as 8 units for one nitrile rubber stock. It is interesting that in the Butyl rubber series four of the six stocks gave good agreement by both methods. It should also be pointed out that agreement or disagreement by the two methods is not

so much a question of the kind of polymer employed as of the stock's creep characteristics which is more a function of the compounding techniques used than of the base polymer. In the series illustrated it happened that all the natural rubber stocks, four of the Butyl stocks and several of the SBR stocks were sufficiently low in creep to give good agreement. Natural rubber stocks are in use which would not give good agreement.
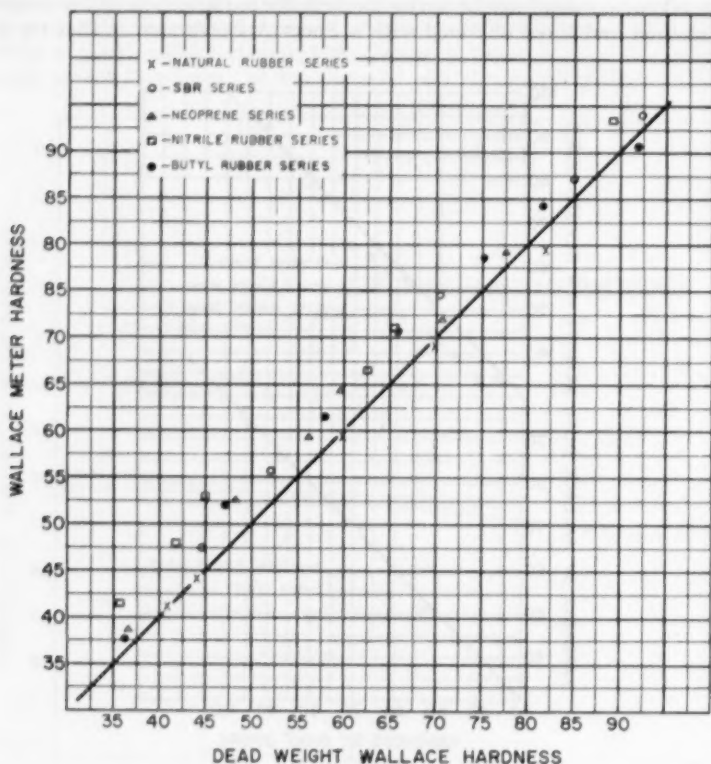
FIG. 4.

The data shown in Figure 3 represent average values obtained in three different laboratories with three different Shore Durometers having a 0.100 inch pin extension and three different Wallace dead weight testers on identical samples which were circulated from one laboratory to another.

One point of this section is to show that agreement between a dead weight instrument using a specified time of reading, e.g., 30 seconds, and an "instantaneous" device such as the Shore A cannot be universally good because of the factor of creep. A further point is that all attempts to establish correlation curves relating dead weight hardness readings to those of pocket meters are doomed to failure unless the correlation is limited to stocks having low or negligible creep.

A corollary of these two points is that if a dead weight instrument meeting the requirements of the proposed ISO method is to be used, as has been suggested, as a standard against which Shore Durometers may be checked the checking must be done only with stocks exhibiting low creep.

THE WALLACE POCKET METER VS. THE SHORE A DUROMETER

The Wallace pocket meter, which gives an "instantaneous" reading as does the Shore A, was designed to give a reading approximately equal to that ob-
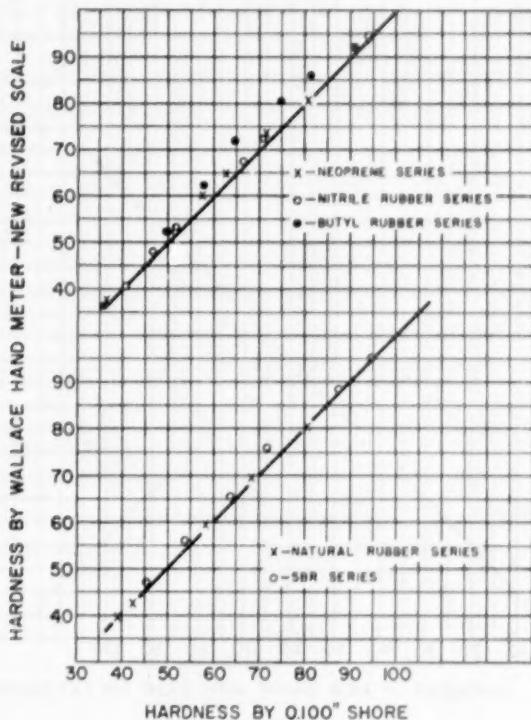
Fig. 5.

tained on the dead weight instrument[2]. This is based on low creep compounds only. Like the Shore A, the Wallace meter gives higher results for high creep compounds than the dead weight tester. Figure 4 illustrates this point.

It would be fortunate if both the Shore A and the Wallace meter responded in the same way, that is, if they would agree with each other when a wide variety of stocks are tested. However, this is not the case as is illustrated in Figure 5. This shows that the stocks in the natural rubber series, several of the SBR stocks, several of the nitrile rubber stocks, and several of the Neoprene stocks agreed well on both instruments but that all the others were off by two to eight units with the Butyl series being the worst offenders.

The reason for this behavior is not known for certain. Since the time interval is virtually the same with both instruments, creep differences cannot be involved. It is thought that the property involved is resilience, with the least resilient stocks giving the higher Wallace reading. The instrument differences responsible for this effect must be differences in friction and inertia in the two instruments.
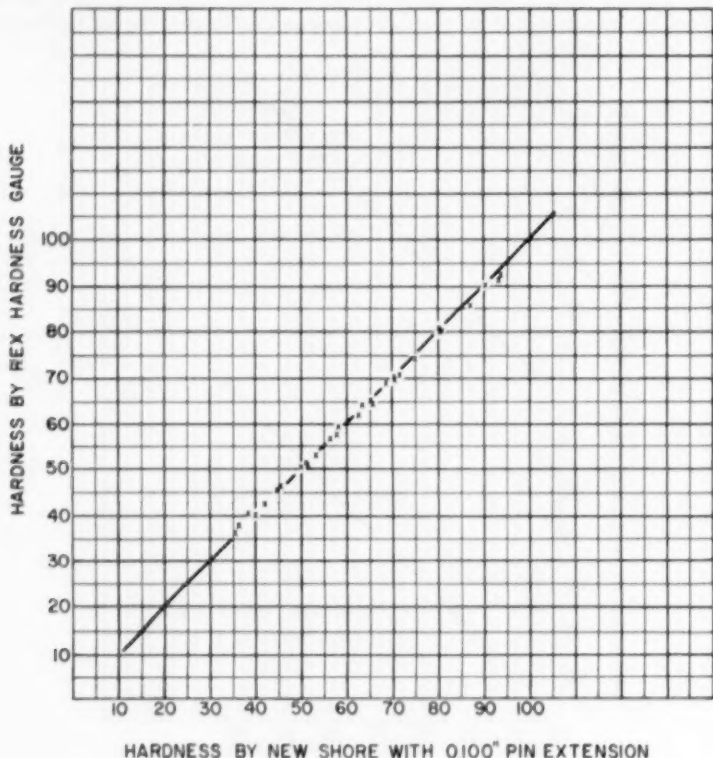
FIG. 6.

It is interesting to note that the Butyl rubber series in the comparison of the Shore A with the Wallace dead weight in Figure 3 indicates low creep by virtue of the good agreement between the values obtained by the two methods but that in Figure 5 the agreement between the Wallace pocket meter and the Shore A is poor. These stocks have very low resilience.

Although high creep and low resilience are generally associated, they may be varied independently.

These data indicate that the new Shore A instrument with a 0.100 inch pin extension will agree with the Wallace pocket meter with the modified ISO scale for a wide range of stocks, but for stocks exhibiting low resilience the agreement will not be good.

COMPARISON OF THE NEW SHORE A DUROMETER
WITH THE REX HARDNESS GAUGE

The Rex Hardness Gauge is described in the ASTM Method D-676 and conforms to the requirements prescribed therein including a pin extension of 0.100 inch. This gauge agrees with the new Shore instrument with the 0.100 inch pin extension as illustrated in Figure 6. The data shown are from tests on a series of stocks based on natural rubber, SBR, Neoprene, nitrile rubber and Butyl.

HARDNESS BY OLD DUROMETERS WITH 0.093" PIN EXTENSION
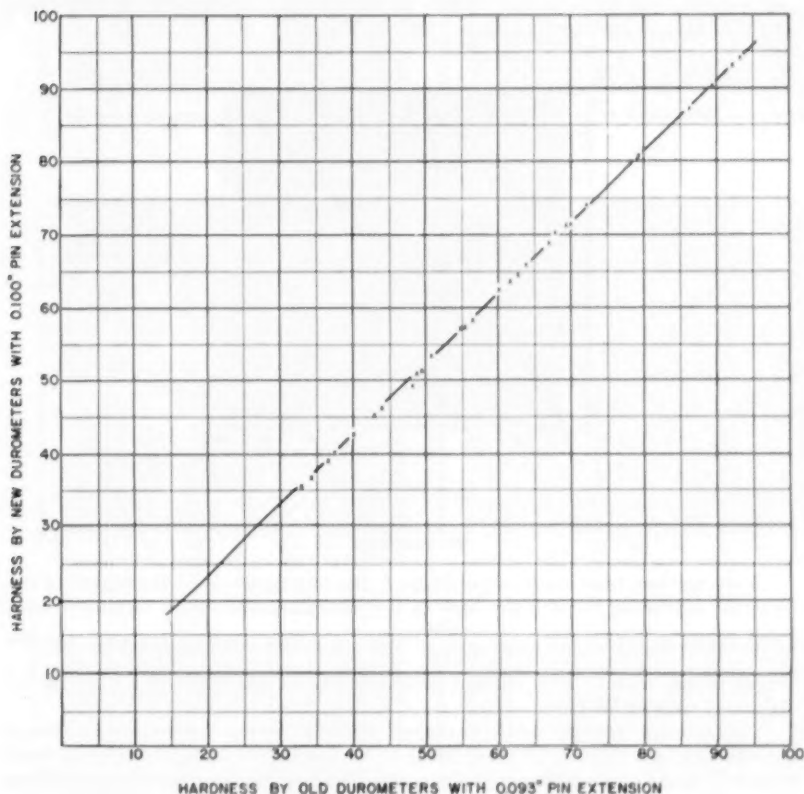
Fig. 7.

WHAT TO DO WITH EXISTING SHORE DUROMETERS
HAVING 0.093 INCH PIN EXTENSION

Since the Shore A scale has been modified by the change in indentor extension and scale expansion, it no longer agrees precisely with the old "effective" Shore A scale. The extent of the differences is shown by the data plotted in Figure 7. The differences amount to about 3 units at the low end of the scale to about 1 unit at 90. This is just enough difference to cause endless confusion

if, for example, a producer uses an old instrument and the consumer checks the product with a new instrument.

It is not possible to fit the old instruments with longer indentors so that their extension would be 0.100 inch since the scale would then be too short. Also it is not possible to adjust the spring loading characteristics to give hardness readings equal to the new instruments over the entire scale.

The simplest and most satisfactory solution appears to be the use of a conversion chart by means of which readings obtained on the old instrument may be converted to the new scale and vice versa. The curve shown in Figure 7 has been redrawn and reduced in size so that it may be reproduced and fitted into the Durometer carrying case. This is Figure 8.
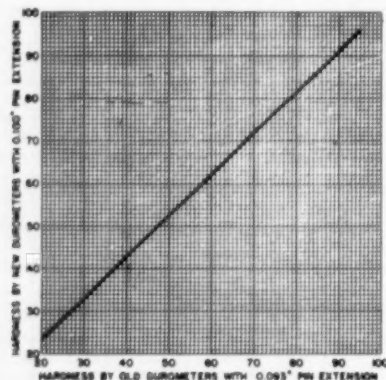
Fig. 8.

SUMMARY

A change has been made in the Shore A Durometer whereby the length of the indentor extending beyond the base of the instrument has been increased from 0.092–0.094 inch to 0.100 inch $^{+.000}_{-.003}$ with a corresponding increase in the length of the scale. This change results in higher readings by 3 units at 30 Dur. to 1 unit at 90 Dur.

This change, together with a change made in the proposed International Organization for Standardization Method for hardness testing, which is a dead weight method, makes the ISO scale and the new Shore A scale agree when stocks of low creep are tested. This will permit the establishment of an international hardness scale, a development much to be desired, and will also permit the use of the ISO method as a check method in the calibration of the Shore A.

With high creep stocks the agreement between the two methods is not good, the new Shore A values being appreciably higher than the dead weight tester values.

The Wallace Pocket Meter with the most recent scale modification also agrees with the new Shore A instrument when stocks of moderately good resilience are being tested, but with stocks having low resilience it reads appreciably higher than the Shore A.
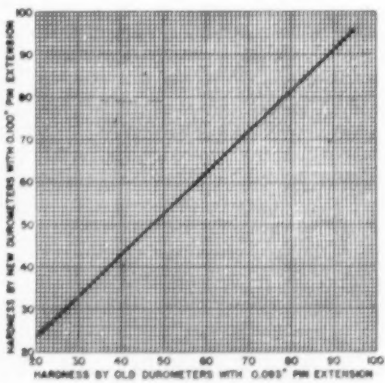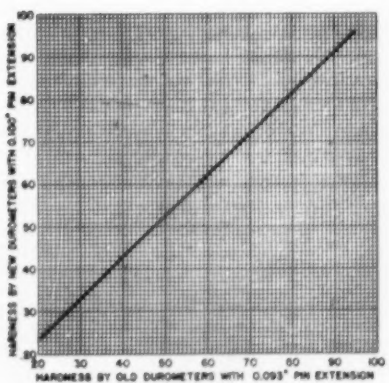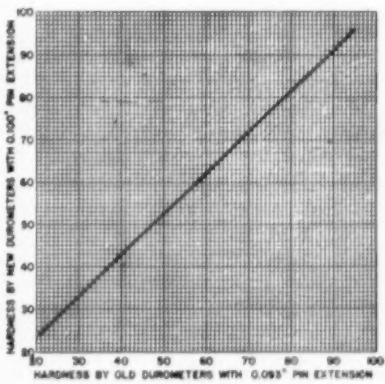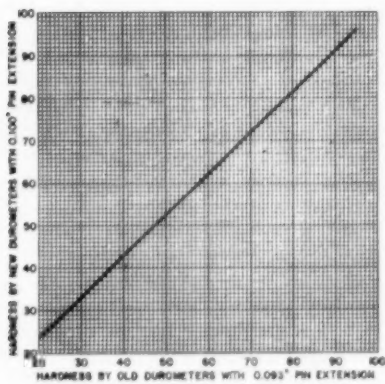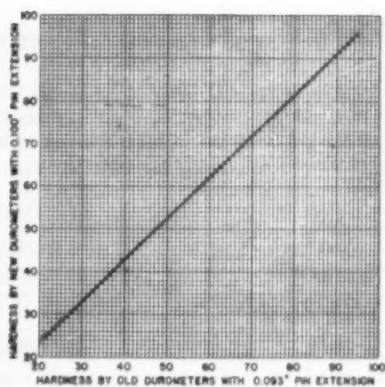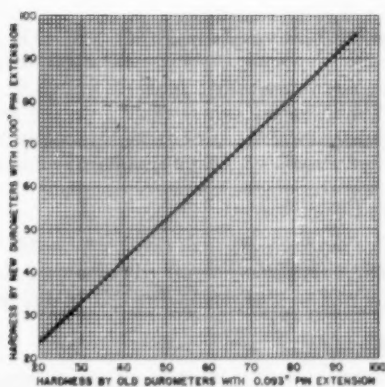
The Rex Hardness Gauge and the new Shore A instrument agree over the entire scale.

Existing Shore A Durometers cannot be modified to read the same as the new Shore. This creates an awkward situation, since thousands of the old Shores are in active use. It is suggested that the conversion curve in Figure 8 be reproduced and be widely distributed to present users of the old instrument.

ACKNOWLEDGMENTS

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GAMMA-RAY VULCANIZATION OF RUBBER*

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INTRODUCTION

Vulcanization is the industrial process which transforms rubber from a soft, sticky, readily molded plastic to the highly elastic material familiar to everyone from innumerable uses. It was discovered by Charles Goodyear in 1839 and was one of the series of crucial inventions which started the United States on its industrial revolution in the nineteenth century. The automotive direction of this industrial development has accentuated the importance of rubber in succeeding years. This year the worldwide product volume to which vulcanization will be applied will exceed two and a half million tons. It is readily understood that vulcanization is now a highly developed process, the resultant of many improvements and developments over the course of a century of competitive use. Goodyear's original conception involved simply the heating of rubber with sulfur. The recognition of the chemical nature of the process was followed by the discovery of materials which, when added to the system, accelerated the reaction tremendously, allowed it to be carried out at lower temperatures, and improved profoundly the physical properties, uniformity, and aging resistance of the rubber. Such chemical vulcanizing systems are now applied in great variety. Many ways are known for vulcanizing rubber without using any sulfur, but they are of relatively minor commerical importance. Some of the synthetic rubbers require rather unique systems for vulcanization. There is continuous, intensive chemical research activity to find still better ways of vulcanizing rubber. So with gamma-ray vulcanization, it will be necessary to show some very tangible advantages to find even a few specialized applications.

The idea of vulcanizing rubber by exposure to energetic radiation is not new. A patent issued to E. B. Newton in 1933 claimed the vulcanization of rubber by short exposures to 250-kV cathode rays[1]. Effects of pile irradiation on uncured elastomers were studied by Davidson and Geib[2]. Numerous investigations of the effects of radiation on the physical properties of plastics are listed in the bibliography prepared by Sun[3]. Gehman and Hobbs[4] observed the vulcanization of rubber by intense gamma radiation. Jackson and Hale[5] measured the physical properties of rubber-filler mixtures as a function of the radiation dose from a strong Co^{60} source for a variety of elastomers. Crosslinking of rubber by pile irradiation was studied in a quantitative way by Charlesby[6]. He emphasized the usefulness of radiation crosslinking as a means for studying the average molecular weight, variation of the gel fraction, and the changes in properties of rubber as the degree of crosslinking is varied.

NATURE OF VULCANIZATION AND THE INTERACTION OF GAMMA RAYS WITH RUBBER

Polymer science teaches that the essential or general feature of all vulcanizing reactions is that they bring about a crosslinking or interconnection of the

long, flexible rubber molecules into a network structure. Thus, a single natural rubber molecule may consist of thousands of small monomer repeating units, (C_5H_8), as indicated in Figure 1. A hypothetical chemical structure for a disulfide crosslink is also indicated. The number of crosslinks required for good technical vulcanization is relatively small, of the order of one crosslink per hundred monomer units. Too many crosslinks destroy the property of high elasticity; too few give excessive plastic flow and permanent set. For good rubber quality it is necessary that in the processing the molecular weight be maintained at a reasonably high value. The free ends of the molecules do not contribute to the strength of the network structure, and hence scissioning or breaking of the long chain molecules has an essentially degrading effect on the properties. Some breakdown of the rubber is required to improve its processability, but, since vulcanization is usually the last step in processing, any molecular-chain scission occurring during vulcanization will generally be undesirable.
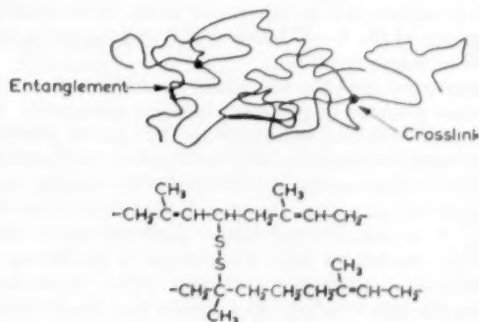
Fig. 1.—Representation of rubber structure.

The exact chemical mechanism or series of reactions involved in chemical vulcanization systems is still very imperfectly known. They are usually considered to be free radical reactions. In general, there occur, besides crosslinking, side reactions and such things as cyclization and chain scission which can affect the quality of the product. Thus gamma-ray vulcanization is not alone as regards the possibility of being accompanied by detrimental side reactions.

The crosslinking action of radiation on polymers has, no doubt, become best known with polyethylene. Here a material with improved properties, especially a higher flow temperature, can be produced. Not all plastics and polymers crosslink under irradiation. Some, such as Butyl rubber, degrade or break down. Whether they degrade or crosslink depends on the chemical structure of the chain molecules. Crosslinking predominates upon irradiation if the polymer has the structure $(-CH_2CH_2-)_n$ or $(-CH_2CHR-)_n$. If the structure is $(-CH_2CR_1R_2-)_n$, degradation is the rule[7]. Polyisobutylene and Butyl rubber come under this classification. Many important types of rubber contain double bonds in the repeating unit and hence are not covered by these generalizations. The isoprene unit of natural rubber (see Figure 1) includes a carbon atom with no hydrogen atom attached. But the presence of the double bond and perhaps the reactive character of the α-methylene hydrogens evidently precludes an extension of the rule to this case.

How radiation brings about the crosslinking of rubber is not known in exact detail. Presumably the general nature of the process corresponds with deductions from the radiation chemistry of simpler systems. The photon energy is degraded, and dissipated eventually in ionization and electronic excitations. The ionized and excited molecules furnish reactive centers which can lead, by a variety of mechanisms, to crosslinking of the rubber molecules. In the broad general picture, since the photon energy is much larger than any of the bond energies, all bonds have about the same chance of being broken. Random bond-fracture is the normal expectation. Usually 20–30 eV are absorbed per broken bond. A probable mechanism of crosslink formation[8] is that the breaking of a C—H bond results in a hydrogen atom which abstracts another hydrogen atom from a neighboring molecule, forming a hydrogen molecule. The resulting two free carbon valencies then unite to form the crosslink. There is reason to suppose that a pair of radicals created by a break in a chain molecule may sometimes recombine. It can be anticipated that vulcanizates containing direct carbon-to-carbon crosslinks will be inherently more stable than sulfur vulcanizates, since the energy of the C—C bond is 58.6 and that of a polysulfide bond only 27.5 kcal./mole, respectively.

It might be suspected that the crosslinks would be concentrated along the paths of the incident photons or particles, but this apparently is not the case. There is experimental evidence, especially in the case of pile-irradiated polyethylene, that the energy-dissipating mechanisms lead to a random distribution of crosslinks[9]. This is presumably most desirable for rubber vulcanizates.

As with chemical vulcanization, there are bound to be some side-effects such as chain scission. It is possible that future work will show that certain radiations or irradiation procedures have advantages in producing a minimum of such degrading effects. Charlesby[6] examined with a mass spectrometer the gas evolved during the pile-irradiation of rubber and found that it was almost entirely hydrogen. From this he concluded that there was very little degradation of the main chains.

The number of molecules directly affected by the incident radiation is presumably rather small. The energy imparted to an atom by the primary radiation is dissipated by secondary collisions and degraded to a level comparable to that absorbed in breaking a chemical bond—about 20–30 eV. These secondary processes are similar, regardless of the character of the incident radiation. Hence, the effects are very much the same for different kinds of radiation and depend principally on the energy absorbed. It is possible that the lower-energy gamma rays from Cs^{137} as compared to those from Co^{60} would suffer more absorption by the photo-electric effect if fillers are present, and hence act somewhat differently for vulcanization. But in the broad, general picture we have at present, such effects have not been recognized. It is to be expected, as the experimental work becomes more refined, that distinctions in the processes may appear due to both the type of radiation and the polymer irradiated.

The radiation absorption processes which result in the vulcanization of rubber may be considerably modified by the presence of particulate fillers, such as carbon black and zinc oxide, usually incorporated in technical rubber compounds to secure desired physical properties. Scattering of the radiation by the particles and the ejection of photoelectrons would tend to increase the effectiveness of the radiation. For gamma rays in the energy range emitted by Co^{60} and fission waste products, the photoelectric effect and Compton scattering are the mechanisms for absorption. Photoelectric absorption accompanied by the ejection of electrons and emission of soft x-rays is appreciable only for

softer gammas, but evidently, even with Co^{60} sources, there is usually a background of soft radiation due to scattering within the source itself[10]. Hence, photoelectric effects cannot be entirely excluded from consideration, especially if there is an inorganic filler, since the cross-section for photoelectric absorption increases rapidly with atomic number. Compton scattering is the principal absorption process for the range of gamma-ray energies in question, and the cross-section is inversely proportional to the photon energy. It depends upon the number of electrons present per cubic centimeter, and hence its relative importance with different fillers can be readily calculated.

Some of the energy considerations involved in gamma-ray vulcanization are very interesting and instructive. From Charlesby's data on pile irradiation of rubber[6] it may be deduced that a gamma radiation dose of 5×10^7 rep cross-links about 1 per cent of the monomer units in rubber. This is a very large dose as compared to those required for many projected uses of gamma radiation. The following doses are representative of those suggested for applications to food processing:

Sterilization of foods[11]	2×10^4 rep
Sprouting control for potatoes[12]	$5-20 \times 10^4$
Insect control in grain[11]	2.5×10^4

This is evidence that a technically satisfactory degree of vulcanization has been secured with doses of gamma radiation in the range from $1-5 \times 10^7$ rep. Assuming that in rubber a rep corresponds to a heat-energy deposition of 93 ergs/gm., 2.5×10^7 rep corresponds to 55 cal./g. This quantity of heat would raise the temperature of a gram of rubber about 200° F if there were no heat losses. Thus the energy input is comparable to the thermal input (assuming no heat losses) required for chemical vulcanization, which is usually carried out at from 275° to 320° F. Of course, the temperature rise during irradiation will be determined by the rate at which the dose is delivered, i.e., the rep/h and the heat losses.

The bond energy in C—C crosslinks is 58.6 kcal./mole, or 9.8×10^{-20} cal. per bond. Estimating that the dose of 2.5×10^7 rep crosslinks 0.5 per cent of the isoprene units, of which there are 8.9×10^{21} per gram, there will then be 4.5×10^{19} crosslinked units per gram, or 2.25×10^{19} crosslinks per gram. The energy in these bonds is $4.5 \times 10^{19} \times 9.8 \times 10^{-20}$ cal., or 4.4 cal. The efficiency of crosslinking in this sense is $4.4/55 = 8$ per cent. That is, the energy in the crosslinking bonds which have been produced is 8 per cent of the energy of the gamma rays which have been absorbed.

The efficiency of crosslinking can also be judged by the energy required to produce a crosslink. The following values are taken from Charlesby's work, using pile irradiation.

Material	eV/crosslink
Natural rubber[6]	44
Polysiloxanes[15]	32
Paraffins[13]	24

The work of Lawton, Balwit, and Bueche[14] on the irradiation of polyethylene with high-energy electrons gave a rather wide range in efficiencies depending upon the molecular weight of the irradiated material. The middle of the range agrees fairly well with the value given above for parafins. A decrease in efficiency was noted with increase in dose, and it was suggested that this might be due to degradation. In a few cases, gamma-ray efficiencies were estimated

for our irradiations of pale crepe rubber, the density of crosslinking being calculated from modulus measurements. The values arrived at ranged from 16 to 100 eV/crosslink.

PROCEDURES

Samples of unvulcanized rubber were sent to the University of Michigan for irradiation by a 3000-curie Co^{60} source[15]. The source consists of a vertical, cylindrical array of aluminum jacketed, activated cobalt rods. The arrangements are such that it can be stored in a water well when not in use and raised by a windlass above the surface of the water for the exposures. The samples were placed in a wire mesh basket permanently mounted in such a way as to be in the center of the cylinder of cobalt rods when the source was raised. Or, alternatively, with lower dose rates, they could be arranged to be at the periphery of the raised source. The arrangements are convenient, in that the samples can be placed in position and removed without remote handling and without having to work under water. The procedure for determining the dose rate of various locations near the source involved the use of ferrous sulfate dosimetry, and has been described[16]. The dose rates used were approximately 2×10^{5} rep/h. There was no heating system in the cave and no control of the temperature during the irradiations. The ambient temperature varied in the tests in the range from 42° to 57° F.

Most of the work was of a survey or screening character to determine the effect of rubber compounding ingredients on gamma-ray vulcanization. The samples were usually small sheets pressed out with a laboratory hydraulic press, platens at about 275° F, to a thickness of about 0.1 in. In some cases, to avoid subsequent shrinkage, it was necessary to clamp the sheets between metal plates at room temperature for about 24 h. Each sheet was then wrapped in 5 mil. aluminum foil. These were assembled in small bundles, wrapped in aluminum foil, flushed with nitrogen to minimize ozone and oxidation effects, and sealed by dipping in molten paraffin. It is known that the presence of oxygen during the irradiation of polymers is quite degrading. We secured much higher tensiles when the samples were clamped individually between aluminum plates similar to the procedure used at Wright Air Development Center[5]. It has not been determined to what extent the improvement was due to molding a better test piece, better exclusion of oxygen, or possibly to the secondary radiation emanating from the aluminum mold. The stress-strain properties of control samples and irradiated samples were measured with an Instron tester[17], using a crosshead speed of 5 in./min. and miniature dumbbells having a neck 0.1 in. wide and about 0.75 in. long.

RESULTS

The addition of the usual chemical vulcanizing agents, including sulfur, did not seem to have much effect on gamma-ray vulcanization. When sulfur was present, no appreciable part of it combined chemically with the rubber, due to the gamma radiation. Experiments in which well-known free radical-producing compounds such as organic disulfides, t-butyl hydroperoxide etc., were added to the rubber, produced, at most, only minor improvements in the gamma-ray efficiency for crosslinking. The addition of fluorescing materials such as anthracene was tried, but again any beneficial effects were small. It is not to be considered that such experiments are complete or that agents will not eventually be found which will influence beneficially the course of gamma-ray vul-
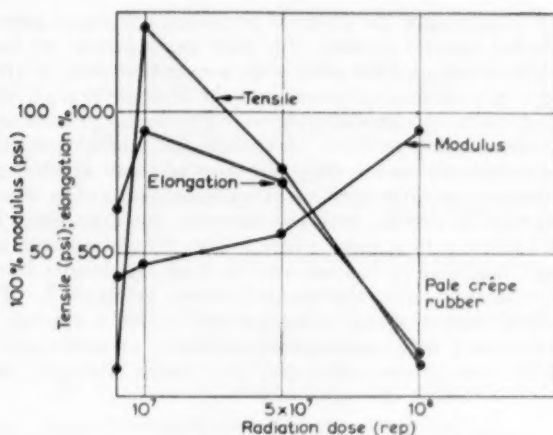
Fig. 2.—Gamma ray vulcanization of rubber.

canization. The future for the process would be markedly improved if the large radiation dose could be materially reduced. The theory and understanding of the process have simply not advanced to a state to say whether this is possible or impossible. Aniline and allyl thiourea have been reported to reduce the degrading effect of radiation on polymethyl methacrylate[18]. This gives some encouragement that the excitation processes are of such a nature that the results can be modified by relatively small amounts of suitable chemicals. Perhaps chemical agents can be found which will increase the crosslinking efficiency of radiation.
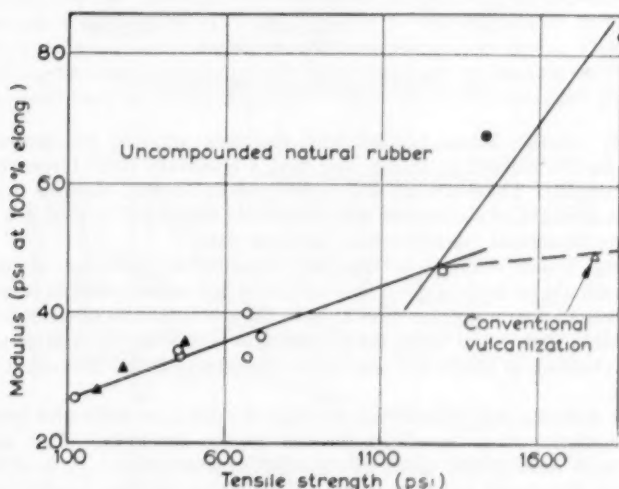
Fig. 3.—Relationship of modulus and tensile strength.

Figure 2 illustrates how the physical properties developed upon irradiation of uncompounded natural rubber. In other experiments, we have reached tensile strengths of about 1900 p.s.i. with a radiation dose of 10^7 rep. The tensile strength is considerably lower than the 3500–3900 p.s.i. which can be reached with chemical vulcanizing systems. This seems to be characteristic of gamma-ray vulcanization to date. Although the tensile strengths are high enough to be technically useful, they fall short of those which can be readily reached by present chemical systems of vulcanization. The tensile strength would be expected to increase with the modulus, but apparently by the time the modulus builds up to a value where a high tensile strength could be expected, enough degradation has occurred to hurt the tensile strength. The course of the modulus-tensile relationship is shown in Figure 3. The point on the plot labelled "conventional vulcanization" is for a typical rubber-gum compound vulcanized with mercaptobenzothiazole as accelerator. For vulcanization with mercaptobenzothiazole, the tensile strength continued to
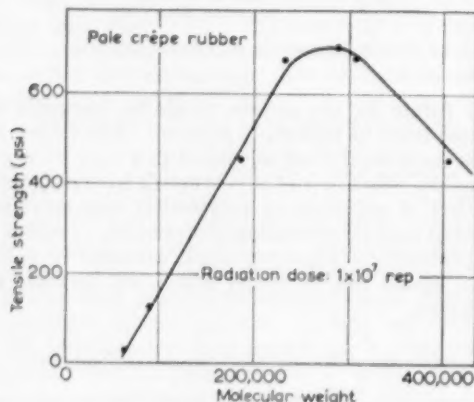
Fig. 4.—Effect of milling on tensile strength.

develop in a rather linear fashion with modulus, whereas the modulus rose abruptly for the highest radiation dose with a relatively small improvement in tensile strength. There are no well developed and tested theories connecting the tensile strength of elastomers with molecular structure, so that it is difficult to give any structural interpretation for these data.

Although tensile strength is frequently regarded as a measure of quality for rubber, it should be kept in mind that rubber is not usually used in tension, and tensile strength does not enter directly into the serviceability of the rubber. It is quite possible that initial lower tensile strength would be offset in service by a superior retention of properties due to the absence of sulfur and other reactive chemicals.

Figure 4 shows that a moderate amount of milling or molecular breakdown before irradiation was beneficial for the tensile strength. The molecular weights were determined from dilute-solution viscosities. It is difficult to understand this result unless it is related to better molding quality and test-piece preparation. Tensile strengths secured with uncompounded GR-S have
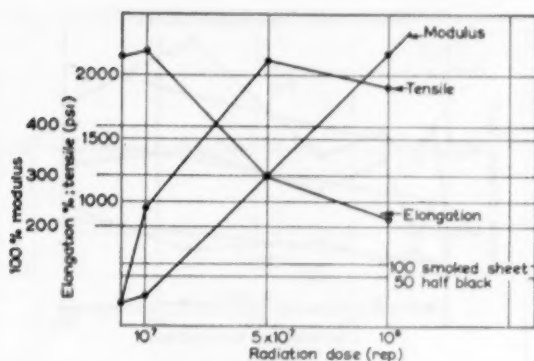
FIG. 5.—Gamma-ray vulcanization of a black masterbatch.

been poor, about 250 p.s.i., which is comparable to values secured with chemical vulcanization. Gamma-ray vulcanization is apparently not able to overcome this inherent structural weakness of GR-S gum stocks. The addition of carbon black to GR-S is required for good tensile strength.

Fillers had more effect on the results with gamma-ray vulcanization than did the usual rubber chemicals. Very good results were secured with mixtures of rubber and carbon black with tensiles well over 2000 p.s.i. for a dose of 10^7 rep. Figure 5 shows the results for one experiment with three radiation doses. It appears that there may be an optimum relation between filler, loading, and radiation dose. The results are evidently related to the radiation scattering effects of the filler particles on the primary radiation.

In Figure 6 are shown data for a series of zinc oxide loadings and a dose of 10^7 rep. In this case, the breakdown of the rubber involved in incorporating the pigment seems to have affected the results, as indicated by the sharp decline in properties with the first addition. Figure 7 presents results from another series of experiments in which three radiation doses were used. The slopes of the lines, representing an average effect for the pigment-loading on the tensile strength, were used to secure Figure 8. Here the tensile strength per unit of
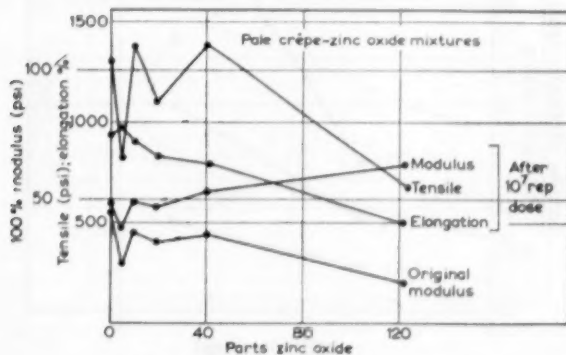
FIG. 6.—Effect of zinc oxide loadings.
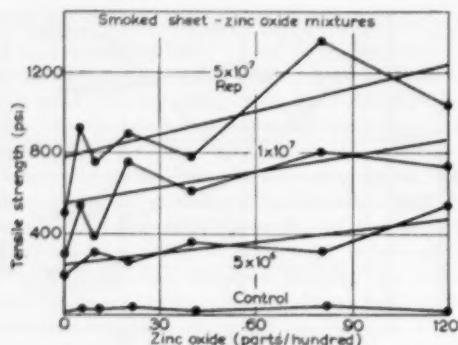
FIG. 7.—Effect of zinc oxide loadings on tensile strength for several radiation doses.

pigment-loading is plotted against the log of the dose to show the regularity which was found in the development of tensile strength with the various pigments. Finally, in Figure 9, the tensile strength per rep per gram of filler is shown to have a linear dependence on the specific volume or reciprocal of the density of the filler. The effects do not appear to be related directly to the Compton scattering. This depends on the number of electrons per cubic centimeter, and calculation shows that for the same loading (weight filler per hundred parts rubber) the number of electrons per cubic centimeter is in the order ZnO, $BaSO_4$, and $CaCO_3$. But the differences in electron density are rather small, only a few per cent between ZnO and $CaCO_2$ loadings. In Figures 7, 8, and 9 scattering of points at the start of the curves is connected with variable mastication in intorducing the pigment.

The modulus data for the same group of samples were treated in a similar manner. From plots of modulus vs. pigment-loading, analogous to those in Figure 7, the modulus increase per unit filler-loading was obtained. A linear
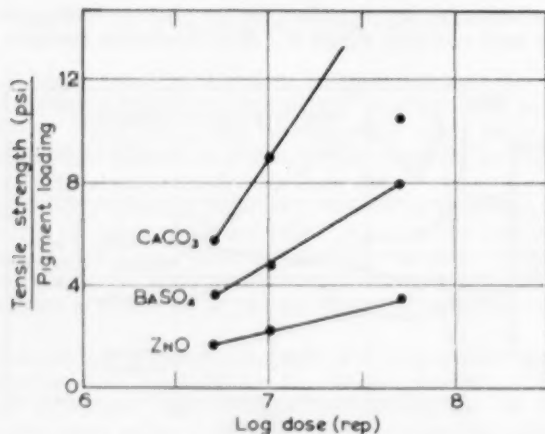
FIG. 8.—Effect of radiation dose on tensile strength.
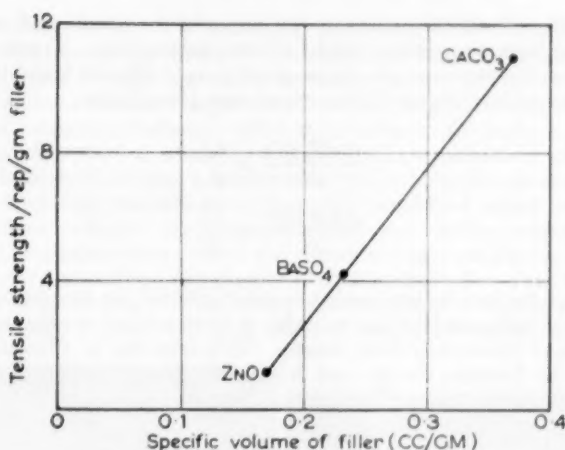
Fig. 9.—Effect of specific volume of fillers on tensile strength per unit of radiation.

relationship existed between tensile strengths and the log of the irradiation doses, but with the modulus data a linear relationship was found with the reciprocal of the radiation dose (Figure 10). The slopes of these lines were found to be related to the atomic number of the metal in the filler (Figure 11). No relationship was noted for these slopes with electron density, specific volume, molecular weight, etc.

The above graphical relationships involving fillers can be expressed in the following equations, which hold over the range of irradiation doses used here.

$$dT/dF = k_1 \log I + I_1$$
$$dM/dF = - k_2/I + I_2$$
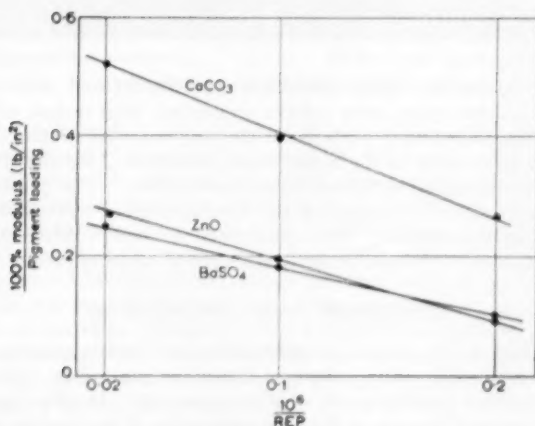
Fig. 10.—Relation of modulus to dose.

where dT/dF and dM/dF represent the slopes of the tensile and modulus vs. filler-loading plots, respectively, and I the irradiation dose. I_1 and I_2 are constants. k_1 and k_2 represent the slopes of the lines in Figures 8 and 10.

The differentiated forms of these equations, given below,

$$\frac{d(dT/dF)}{dI} = \frac{k_1}{I}$$

$$\frac{d(dM/dF)}{dI} = \frac{k_2}{I^2}$$

indicate that the irradiation process is most efficient for low doses of gamma rays. It also indicates that the modulus is more subject to efficiency decrease with increased irradiation than tensile. This lowering in efficiency has also been noted by Lawton, Balwit, and Bueche[10] with polyethylene.
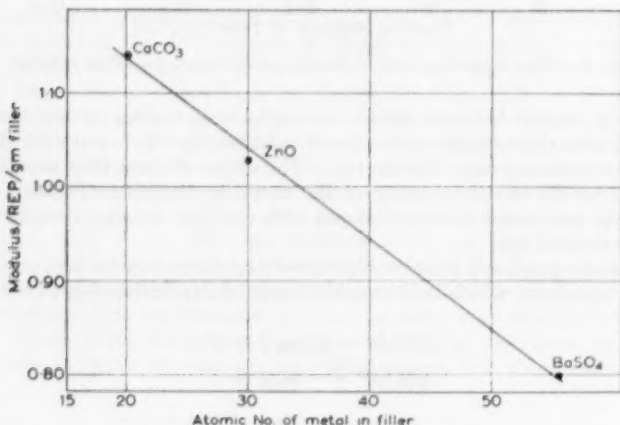
Fig. 11.—Relation of atomic number of filter to modulus per unit of radiation.

Figure 12 shows the x-ray diffraction pattern secured with a sample of slightly broken-down pale crepe rubber irradiated with a dose of 10^7 rep, as compared to the amorphous pattern for the unirradiated control sample. No crystallinity was evident in the latter case, presumably because of the plastic flow and stress relaxation in the uncrosslinked rubber. The radiation induced crosslinks acted normally in assisting the development of a crystalline structure upon stretching the rubber. The occurrence of such a fiber structure is a contributing factor to the good tensile strength of natural rubber.

DISCUSSION AND CONCLUSIONS

In concluding, a few general considerations involved in gamma-ray vulcanization will be discussed. Any industrial future for gamma-ray vulcanization is tied in with further developments of atomic energy. It offers another possibility for the constructive use of the huge quantities of radioactive wastes which are expected to materialize when an appreciable fraction of power requirements

is met by atomic energy. It is, therefore, dependent on the economy with which such wastes can eventually be processed and handled.

The huge dose required for vulcanization, 1 to 5×10^7 rep is of a higher order of magnitude than that required for food and drug sterilization and similar applications for gamma radiation which seem to be on the horizon. The only feasible way at present to secure such doses in large volumes of material in a reasonable time short of using a reactor itself would be to use spent reactor fuel elements. Such fuel elements are presumably capable of supplying a dose of 10^7 rep in about an hour. As mentioned at the start, if this dose is taken in a short period, the temperature rise of the rubber will be considerable, and might reach ordinary vulcanizing temperatures of 275°–300° F. This suggests at once that a combination of crosslinking due to radiation and some chemical vulcanization might provide a most efficient system for using the radiation.

(a) Stretched before irradiation. (b) Stretched after irradiation, 10^7 rep.
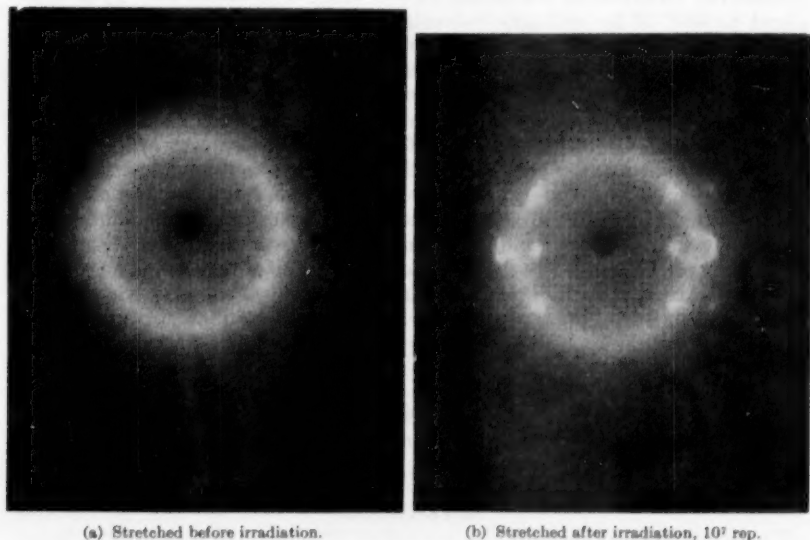
Fig. 12.—X-ray diffraction patterns of pale crepe rubber, 500% elongation.

Furthermore, the heat should be sufficient to permit the molding of the rubber. The vulcanization could conceivably be carried out in steel molds, since ¾ inch of steel would reduce the intensity of 1-MeV gammas only about 50 per cent. Another rather obvious procedure would to to mold the articles and give them enough conventional cure to permit their removal from the mold. The cure could then be completed by irradiation. One of the advantages of gamma-ray vulcanization would be that thick rubber articles, even up to a foot or more thick, could be vulcanized uniformly and as rapidly as a thin sheet. It would require about 35 hours to vulcanize a 1-foot thick rubber press pad by conventional thermal conductivity heat-flow with the surfaces at 250° F, and then there would be a difference by a factor of about 6 between the extent of the cure at the center and at the surface.

It is quite possible that ways will be found to reduce the radiation dose required for vulcanization. Special types of synthetic rubber may be developed

which are particularly susceptible to radiation crosslinking. But, in practically every case, gamma-ray vulcanization will be in competition with a chemical process which has undergone a hundred years of intensive development. Anything so new and unexplored will certainly have to experience a large amount of research and development before it can reasonably be expected to find many applications. But it is not proper to look at all the difficulties without mentioning some of the interesting new possibilities opened up by gamma-ray vulcanization. These include possibilities of developing new types of rubber which cannot be readily vulcanized by chemical systems, and this chemical inertness, in turn, could be reflected in superior aging stability and resistance to high temperature. The likelihood of producing rubber with much better heat-resistance and aging properties has already been mentioned, and, in fact, has been experimentally established in several cases[1,5,19]. The smearing temperatures[20] for our gamma-ray vulcanizates containing carbon black were about 500° F, as compared to 400° F for ordinary vulcanizates. Cold gamma-ray vulcanization should permit the vulcanization of extruded or preformed shapes without the distortion which would occur due to heating. Likewise, metal-bonded rubber units would be free of the internal stresses which occur due to shinkage of the rubber after vulcanization. Preliminary milling, processing, and extruding of the rubber stock could be carried out faster at higher temperatures if no vulcanizing ingredients were present, and this might help to compensate for higher vulcanization costs. Thus gamma-ray vulcanization has a number of unique features, and it is not too much to hope that some of its possibilities will eventually find a place in industrial vulcanization. But this appears to be a long-range project related to the abundant production of fission-waste products, their utilization, and the growth of the technology of working with intense radiations.

ACKNOWLEDGEMENTS

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THE REACTION MECHANISM OF THIURAM DISULFIDE VULCANIZATION OF POLY-1,5-DIENES, PARTICULARLY OF NATURAL RUBBER *

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In previous publications on thiuram vulcanization[1] we confined ourselves to the presentation and discussion of our extensive experimental work. We had investigated quantitatively the conversion of thiuram disulfides and were in a position to describe the kinetics of thiuram vulcanization. Such investigations are, of course, of particular value to technology for information about the rate and temperature dependence of vulcanization reactions. Our experiments were therefore not primarily designed to determine the details of reaction mechanism, which we had hitherto treated with restraint, and experience shows that the study of reaction kinetics does not always provide the key to a complete solution. All the same, it now seems reasonable to pick out some of the results we have obtained, and so consider the question of a reaction mechanism for thiuram vulcanization. We should, however, like to state, that although the present treatment concerns matters which may include some pertinent points, it does not necessarily represent a final interpretation.

It is to be stressed, that any postulated reaction mechanism must explain what we regard as a stoichiometrical, i.e., concentration and temperature independent conversion of thiuram disulfide to zinc dithiocarbamate. The following experimental results thus formed the basis of our considerations[2]:

1. On vulcanization of natural rubber, Buna, or even on reaction with geraniol, the limiting yield of dithiocarbamate amounted to two-thirds of the thiuram disulfide taken and was practically independent of temperature, concentration, and substituent groups of the thiuram disulfide.

2. On vulcanization of natural rubber with tetramethylthiuram monosulfide and sulfur (1 gram atom of sulfur per mole of thiuram monosulfide) there also occurred a two-thirds conversion of thiuram monosulfide to dithiocarbamate.

3. A relatively very slow and, as regards vulcanization, "indifferent" reaction of thiuram monosulfide with rubber produced zinc dithiocarbamate in the presence of zinc oxide.

4. Limiting yields of dithiocarbamate higher than 66 mole per cent were observed when an excess either of sulfur or of thiuram monosulfide was taken, i.e., their ratio was greater or less than 1 gram atom of sulfur to 1 mole of thiuram monosulfide.

5. On vulcanization by means of thiuram monosulfide and sulfur at temperatures below 120° C, the rate of formation of dithiocarbamate was governed

by the prior reaction of the thiuram monosulfide with sulfur having an activation energy of 30 kcals.

6. At no stage of vulcanization by means of thiuram monosulfide and sulfur could any thiuram disulfide be identified in the rubber, although vulcanization, as measured by the two-thirds conversion to dithiocarbamate, proceeded as if the thiuram disulfide had been used instead of monosulfide plus sulfur.

At a time when our knowledge of vulcanization was less exact, we felt inclined to follow the views of A. Jarrijon[2], according to which thiuram disulfides give rise to carbon-carbon crosslinking. We thought that thiuram disulfides enter the reaction in the form of dithiocarbamate radicals, $R_2N-C(S)-S*$, producing both dehydrogenation at the α-methylenic position as well as reaction at the double bond, but in this way we were not able to explain the two-thirds yield. We could not then subscribe to the reactions of thiuram vulcanization discussed by D. Craig and others[4]. In the meantime, however, we have come to believe that the concepts which these authors have expounded are correct in so far as they call for sulfur crosslinkages in polyisoprene.

As a starting point in developing a reaction mechanism for thiuram vulcanization we shall assume, that thiuram mono- and disulfides react via radicals, but the formulation of corresponding equilibria shall merely express modes of reactivity inherent in the molecules. They are shown in the following reaction mechanism by Steps (1), (2) and (3).

Schematic Reaction Mechanism

(1) $R_2N-C(S)-S-C(S)-NR_2 \rightleftharpoons R_2N-C(S)-S* + R_2N-C(S)*$

(2) $R_2N-C(S)-S-S-C(S)-NR_2 \rightleftharpoons 2 R_2N-C(S)-S*$

(3) $R_2N-C(S)-S-S-C(S)-NR_2 \rightleftharpoons R_2N-C(S)-S-S* + R_2N-C(S)*$

(4) $\cdots CH_2-\overset{\overset{\textstyle CH_3}{|}}{C}=CH-CH_2\cdots + R_2N-C(S)-S* + R_2N-C(S)* \longrightarrow$

   $\cdots \overset{\overset{\textstyle CH_3}{|}}{CH}-\overset{}{C}=CH-CH_2\cdots + R_2N-C(S)-SH \longrightarrow$ zinc dithiocarbamate

   $\overset{|}{R_2N-CS}$

(5) $2\cdots CH_2-\overset{\overset{\textstyle CH_3}{|}}{C}=CH-CH_2\cdots + 2 R_2N-C(S)-S-S* \longrightarrow$

   $2\cdots \overset{\overset{\textstyle CH_3}{|}}{CH}-C=CH-CH_2\cdots + 2 R_2N-C(S)-S*$

   $\overset{|}{SH}$

(6) $2\cdots CH-C=CH-CH_2\cdots + 2 R_2N-C(S)-S* \longrightarrow$

   $\cdots \overset{\overset{\textstyle CH_3}{|}}{CH}-C=CH-CH_2\cdots$

   $\overset{|}{S}$

   $\overset{|}{S}\quad\overset{\overset{\textstyle CH_3}{|}}{}$ $+ 2 R_2N-C(S)-SH \longrightarrow$ zinc dithiocarbamate

   $\cdots CH-C=CH-CH_2\cdots$

$$(7) \quad 3\ R_2N{-}C(S){-}S{-}S{-}C(S){-}NR_2 + \quad 4\cdots CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH{-}CH_2\cdots + 2\ ZnO$$

$$2\ Zn(S{-}C(S){-}NR_2)_2 \qquad + \qquad 2\cdots CH{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH{-}CH_2\cdots + 2\ H_2O$$
$$R_2N{-}CS$$

$$+ \qquad \begin{array}{c} CH_3 \\ \cdots CH{-}C{=}CH{-}CH_2\cdots \\ | \\ S \\ | \\ S \quad CH_3 \\ | \quad | \\ \cdots CH{-}C{=}CH{-}CH_2\cdots \end{array}$$

$$(8) \quad R_2N{-}C(S){-}S{-}C(S){-}NR_2 + S_4 \longrightarrow R_2N{-}C(S){-}S_3{}^* + R_2N{-}C(S){-}S^*$$

In Step (4) we formulate the "indifferent" reaction of thiuram monosulfide with rubber, and Step (5) shows the attack of trithio radicals on allyl units of the polyisoprene leading to the formation of a mercaptan. In Step (6), reaction of the resonance stabilized dithiocarbamate radicals of (5) with the mercapto groups gives dithiocarbamic acid, which—here not separately shown—is converted into zinc dithiocarbamate, and produces a disulfide crosslink.

The continuous removal of trithio radicals formed in Step (3) necessarily leaves the radicals $R_2N{-}C(S)^*$, consumed in Reaction (4). The dithiocarbamate radicals required for this are furnished by the symmetrical dissociation of thiuram disulfide in Step (2), which we also consider possible.

It should be noted, that on summation altogether three moles of thiuram disulfide enter into the overall Reaction (7). Two of these are converted into dithiocarbamic acid and consequently into zinc dithiocarbamate. One remains combined in the rubber, two of its sulfur atoms forming the disulfide crosslink and the other two being part of the $R_2N{-}C(S)^*$ radicals attached to α-carbon atoms.

The above reaction mechanism for thiuram vulcanization can thus at least explain the stoichiometrical two-thirds yield of zinc dithiocarbamate from the thiuram disulfide. This is easy to see, because it shows how one reaction is consequent upon another, e.g., as the reaction with allyl units removes trithio radicals from Equilibrium (3), a corresponding number of $R_2N{-}C(S)^*$ radicals must be formed. Of course, when a thiuram monosulfide alone is present in rubber, they are obviously produced only very slowly and lead to the formation of dithiocarbamate by the "indifferent" reaction according to (4). If, however, thiuram disulfide is added to rubber, they must be produced in the measure and quantity in which trithioradicals are consumed, and so ensure a quicker turnover of $R_2N{-}C(S)^*$ radicals in Reaction (4). This in turn calls for further dithiocarbamate radicals which can be taken from Equilibrium (2). It will be realized, that all this constitutes a self-contained course of reactions, as is required by the results of our quantitative investigation of the chemical changes as well as of the observed kinetics. There exists in no way any necessity for a temperature dependence of the overall reaction mechanism.

Considering now vulcanization by means of thiuram monosulfide and sulfur

(1 gram atom sulfur per mole of thiuram monosulfidde), a reaction preceding that of vulcanization became clearly noticeable at temperatures below 120° C and governed the rate of dithiocarbamate formation. By analogy with the ideas developed by H. Krebs and M. Gordon[5] let us assume, that this process consists of the opening of the S_8-ring by thiuram monosulfide as indicated in Reaction (8).

When one gram atom of sulfur is apportioned to each mole of thiuram monosulfide, at first only one-eighth of the thiuram monosulfide is used in Reaction (8). The polythio radicals so produced will subsequently degenerate both by reaction with allyl units as well as by sulfur transfer to the remaining thiuram monosulfide. The overall changes are in fact the same as those obtained on vulcanization with thiuram disulfide, while it is evident, that the disulfide itself need not be detectable. Thus, thiuram monosulfide opens the S_8-ring and initiates a cycle of reactions in the same way as this occurs in other cases, e.g., with organic bases; whether it involves an ionic or a radical mechanism is for the moment immaterial. In the sense of these considerations we look on a thiuram disulfide as a molecule, which already embodies the innate reaction cycle.

Having regard to crosslinking, there exists of course the possibility, that the mercaptan produced in Reaction (5) can add to the double bond of an adjacent allyl unit and give a crosslink of the monosulfide type. If this were to apply, then no dithiocarbamate would be formed and moreover such a reaction would not be in agreement with the results of E. H. Farmer and others[6]. According to them the reaction of a model substance with thiuram disulfides in the presence of zinc oxide produced dialkenyl sulfides. Such sulfides, however, are formed in Reaction (6).

With this account a reaction mechanism for thiuram vulcanization has been put forward for discussion. It accounts to a considerable degree for the quantitative results of chemical change, although further investigation will be necessary to show whether it constitutes a really exhaustive interpretation. In particular, research on the constitution of the products formed when thiuram compounds react with model substances will have to provide further material for this discussion. The present contribution is therefore intended to stimulate the reader and not as a fully substantiated representation of the mechanism of thiuram vulcanization.

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STRUCTURAL CHARACTERISTICS OF THE SULFUR LINKAGE IN NATURAL RUBBER VULCANIZATES *

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INTRODUCTION

The vulcanization of rubber is now recognized as a process in which the linear molecules of the parent hydrocarbon are crosslinked by primary valency bonds to produce a network structure. The supporting evidence is of three kinds: (1) the molecular coupling of simple analogs of rubber on reaction with vulcanizing agents; (2) the parallelism between the fission of chemical bonds in simple organic sulfur compounds and the degradation of sulfur vulcanizates; and (3) the success of the theory of rubberlike elasticity, which is based on the network model of the vulcanized state, and which now gives quantitative expression to elastic, swelling and related properties[1,2]. As regards (1), we would direct attention particularly to the action of di-*tert.*-alkyl peroxides, which readily couple simple olefins via α-methylenic carbon atoms[3] and effect vulcanization of rubber under similar conditions[4,5], and to the olefin-coupling and vulcanization effected by *dis*-azodicarboxylates[1,6] and *dis*-thiolacids[7,8], whereas their monofunctional counterparts, though profoundly modifying the rubber, do not produce a vulcanizate. Evidence under (2) includes (a) the degradation of certain types of sulfur vulcanizates by means of methyl iodide[9] which causes the fission of C—S bonds (equivalent to sulfur crosslinks) in specific types of organic monosulfides[9,10,11]; (b) the solubilization of mercaptobenzothiazole (MBT) and diphenylguanidine (DPG) accelerated vulcanizates by reaction with lithium aluminum hydride[12] treatment which is known to sever S—S links in simple dialkyl di- and polysulfides[13]; and (c) the solubilization of a tetramethylthiuram disulfide (TMT)-accelerated butyl vulcanizate by hydrogen sulfide at 149° C[14], and the degradation of a natural rubber-sulfur vulcanizate by *n*-butane thiol at 140° C[15], effects associated with hydrogen-transfer processes $(RS \cdot SR + R'SH \rightarrow RSH + RSSR')$ between di- and polysulfide crosslinks in the vulcanizate $(RS \cdot SR)$ and the degrading agent $(R'SH)^{c/16}$.

Notwithstanding these observations, the scantiness of our knowledge of the detailed chemistry of sulfur vulcanization forms a severe contrast to the extensive technological background. Until recently the structural characteristics of the sulfur crosslinkage, i.e., the number of sulfur atoms in the crosslink, the hydrocarbon structure at the site of sulfur attachment, and the variation of these features with vulcanizing conditions, all remained obscure. The realization of the physical act of vulcanization with such a wide variety of reagents—sulfur and non-sulfur-containing alike—indicates that no great specificity is involved between network-type and elastic behavior, but it is equally

clear that certain other important properties (e.g., aging characteristics, thermal stability) are not similarly insensitive.

Our tactical approach to this problem is based on the opinion that conventional vulcanizing systems are far too complex to be studied directly; the large number of components greatly magnifies the reaction possibilities, and in conjunction with the physical state of the vulcanizate presents excessively difficult analytical problems. Moreover, the use of tensile and other physical properties for elucidating network-type is of little value as it affords only a composite picture of the over-all chemical changes, and is necessarily inadmissible when it is desired to establish the correlations on which its usage fundamentally depends. Accordingly, it appeared necessary to study first the sulfuration of simple olefins, structurally related to the natural rubber hydrocarbon. Apart from the much greater probability of resolving these reactions, the separation and characterization of the products permit analytical methods to be devised which can be employed diagnostically in the physically less tractable vulcanizates.

NATURE OF THE POLYISOPRENE–SULFUR REACTION AT 140° C

Previous investigations[17-19] of the reaction of mono-olefins with sulfur at about 140° C indicated that the products were polysulfides RS_xR' in which x averaged four and in which R and R′ were apparently alkyl and alkenyl groups, respectively. Farmer and Shipley[19] made the further important finding that 1,5-diolefins (as in polyisoprenes including natural rubber) react with sulfur under vulcanizing conditions both (1) intramolecularly to give cyclic sulfides, and (2) intermolecularly to give crosslinked sulfide units. Detailed knowledge of these structures is of importance, since the presence of the former reflects inefficient crosslinking and may well modify the physical properties of a vulcanizate by producing irregularities in the network, while the structure of the crosslinked sulfide unit may be important in determining the service life (e.g., thermal and oxidative stability) of the vulcanizate.

We have now identified the cyclic sulfides formed during the reaction of the di-isoprene 2,6-dimethylocta-2,6-diene, $Me_2C:CH \cdot CH_2 \cdot CH_2 \cdot CMe:CH \cdot Me$, with sulfur at 140° C, viz., I–IV. Their characterization has been based mainly on their infrared and ultraviolet absorption spectra. For example, infrared absorption at ca. 890 cm.$^{-1}$ indicated the presence of $CH_2:CR_2$-type unsaturation, which was shown to be due to III by catalytic hydrogenation of a fraction free from I (obtained by chromatographic separation on silica gel) to a saturated sulfide identical with a synthetic specimen of II. The presence of I and II was established by infrared absorption bands identical with those characteristic of synthetic I and II[20]. The presence of IV was based on (a) the observed ultraviolet light absorption maximum at 2290 to 2300 Å., which is also found in the synthetic cyclic sulfide V[21], and is identified with the C=C—S chromophore; and (b) the removal of I, II, and III by a chromatographic procedure to leave a fraction having no absorption in the infrared attributable to an unsaturated grouping (the tetra-substituted type is undetectable) but which on catalytic hydrogenation absorbed 1 mole of hydrogen per $C_{10}H_{18}S$ unit to give pure II.

The proportions of I–IV are dependent on the reaction period. After 5 hours at 140° C the major component was III (50%), together with IV (25%) and some II, while I was substantially absent. This material also showed max-

I   II   III

IV   V
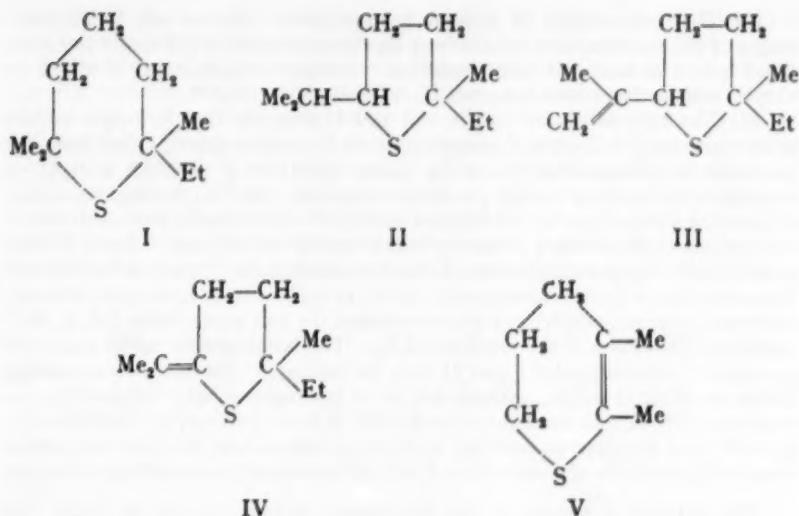
imum ultraviolet absorption at 2730 Å., ϵ, 4400 which is provisionally attributed to ca. 10 per cent of a highly conjugated compound having the chromophore $C:C\cdot C:C\cdot \overset{S}{C}$ or $C:C\cdot C\cdot C:C$.   Prolonged heating (50 hours at 140° C) yielded a cyclic sulfide fraction comprising I (60%), some II, III (4%), and IV (31%), but free from the conjugated material referred to above.

These observations lead to the following conclusions concerning the mechanism of the polyisoprene-sulfur reaction at 140° C.

(1) The cyclic sulfide III results from a *primary* intramolecular sulfuration of the olefin, involving attack by sulfur at the unmethylated end of a double

$$\cdots (\text{I})$$

III
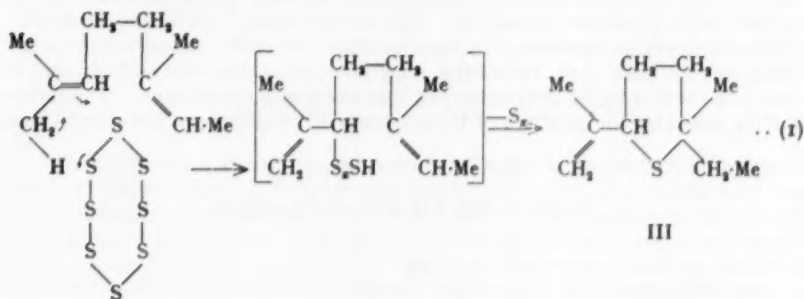
bond (cf. van Veersen[22]); followed by cyclization of an intermediate mercapto-compound (Reaction 1).   This mechanism is in contrast to the previous conclusions of a free-radical attack of sulfur at α-methylenic groups[19,23], but is consistent with the polar mechanism proposed for the substitutive chlorination of mono-olefins[24] and polyisoprenes[25].

(2) The cyclic-sulfide IV appears in appreciable amount only in the later stages of the reaction, and results from the isomerization of III under the combined action of heat and sulfur-catalysis. Similar isomerizations of allylic to vinylic sulfides have been reported by Tarbell and McCall[26].

(3) The fully saturated nature of I and II suggests that hydrogen sulfide is an important auxiliary sulfurizing agent, its formation arising either from the oxidation of intermediate thiols by sulfur ($2RSH + S \rightarrow RSSR + H_2S$)—a reaction which simultaneously produces a crosslink—or from the decomposition of primarily formed labile crosslinked sulfides[19]—with consequent destruction (reversion) of the network structure in the case of vulcanizates. I and II may result directly by polar addition of hydrogen sulfide to the parent olefin followed by cyclization of the intermediate *tert.*-thiol, or indirectly by hydrogen exchange between hydrogen sulfide and the crosslinked di- and polysulfides (cf. p. 397) and then cyclization of the resultant thiol. The latter process again manifests reversion. Alternatively, I and II may be formed by thermal decomposition of the crosslinked sulfide, without release of hydrogen sulfide, followed by abstraction of hydrogen from the parent olefin to form thiols which subsequently cyclize[27], but this process, contrary to previous supposition, does not necessarily result in destruction of crosslinks and is thus inadequate in explaining reversion.

The detailed structures of the crosslinked sulfides are still in doubt, but substantial advances have been made towards their characterization. Thus, they do not, as was originally visualized[19,22], contain solely open chain di-isoprene units linked in an alkyl-alkenyl polysulfide structure, but *cyclic* structures of types II and IV are also incorporated at points adjacent to the sulfur crosslink. This follows from the low degree of unsaturation as revealed by infrared analysis, and from the results of hydrogenolysis. After a 5-hour reaction period only 0.6 double bonds per C_{20}-unit of $R_2C:CHR$ and 0.12 double bonds per C_{20}-unit of $CH_2:CR_2$ type unsaturation was present (cf. 3 double bonds per C_{20}-unit required for an alkyl-alkenyl polysulfide derived from the di-isoprene), and the proportion of these unsaturation-types is further reduced after 50 hours (0.35 double bonds of type $R_2C:CHR$ and 0.04 double bonds of type $CH_2:CR_2$ per C_{20}-unit), reflecting an increase in the proportion of saturated cyclic sulfide units. The hydrogenolysis of the crosslinked material with lithium aluminum hydride leads to similar conclusions. The 5-hour product, analyzing for RS_6R', yields considerable amounts of hydrogen sulfide (indicative of polysulfide crosslinks) and an open chain monothiol, which on cyclization with sulfuric acid is converted into a cyclic sulfide having I as the major component. The latter finding indicates the presence of the grouping VI containing a *tert.*-alkyl C—S

$$
\begin{array}{cc}
\text{Me} & \text{Me} \\
| & | \\
\text{R·CH}_2\text{·C·CH}_2\text{·CH}_2\text{·CH}_2\text{·C:CH·CH}_2\text{·R} \\
| \\
\text{S} \\
| \\
& \text{VI}
\end{array}
$$
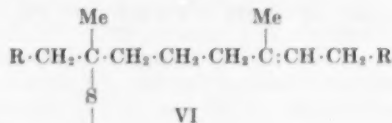
link in the polysulfide. The presence of dithiols in the reduced products shows that structures of the type $RS_xR'S_xR''$ occur in the crosslinked material, and similar repetition of the crosslinking process has been detected in mono-olefin sulfurations. Hydrogenolysis of the 50-hours' product, analyzing for $RS_{3-4}R'$, liberated no hydrogen sulfide, indicating the absence of polysulfidic crosslinks, $-S_x-$ ($x > 2$). Two distinct products resulted from this treatment: (i) a

material $C_{10}H_{18}S_2$ (1 SH group/mole) consisting of VII and, or VIII, and IX; and (ii) a crosslinked fraction $C_{20}H_{40}S_3$ devoid of thiol groups.   This combined evidence shows that the original crosslinked material obtained on prolonged heating contains structures typified by, though not necessarily identical with, X and XI, the crosslink being solely by —S_1— and —S_2— units.   It is significant that infrared analysis of ebonite revealed a band at 947 cm.$^{-1}$ of similar shape and intensity to one at 945 cm.$^{-1}$ in the above crosslinked material and XII[20] (see below).   This band appears to be related to the 958, 942 cm.$^{-1}$ doublet in II and to the 947 cm.$^{-1}$ band in VIII but not to *trans*-R·CH:CH·R groups as believed by Sheppard and Sutherland[28], and thus strongly suggests the presence of cyclic structures such as II, possibly associated with XII, in ebonite.
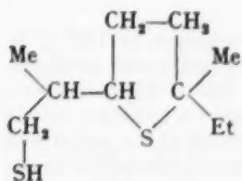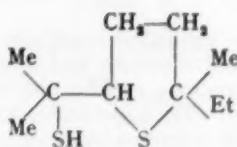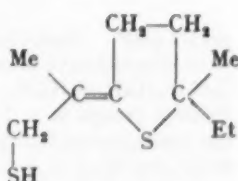
VII   VIII   IX
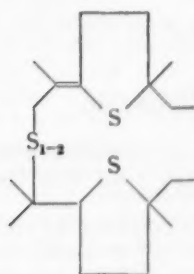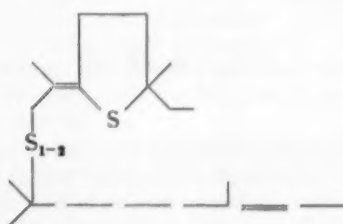
X   XI

INFLUENCE OF SULFURATION CONDITIONS ON PRODUCT COMPOSITION

When the above sulfuration process is conducted in the presence of an amine such as diethylamine, both hydrogen sulfide and sulfur play major roles and their combined action in the case of 2,6-dimethylocta-2,6-diene leads not only to the cyclic sulfides I–IV, but also to crosslinked material composed mainly of the fully *saturated* structure XII in which mono- and disulfide crosslinks predominate[20].   Such structures should confer upon the vulcanizate both increased thermal and oxidative stability, due (i) to the increased stability of mono- and disulfides as compared with polysulfides; (ii) to the di-*tert*.-alkyl nature of the crosslink; and (iii) to the absence of unsaturation vicinal to the sulfide groups.

The mechanism of the amine-promoted sulfuration has been revealed by studying the reactions with cyclohexene, 1-methylcyclohexene, and 2-methyl-

XII
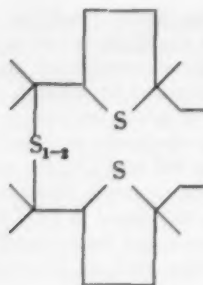
pent-2-ene[29]. Diethylamine and sulfur react with cyclohexene at 140° C to yield dicyclohexyl mono- and disulfides and saturated polymeric products, $C_6H_{11}S_x(C_6H_{10}S_x)C_6H_{11}$, containing cyclohexane units linked by mono- and disulfide groups ($x = 1 - 2$). The major sulfurating agent is hydrogen sulfide (as diethylamine hydrosulfide), formed by prior interaction of the sulfur and amine according to Reaction 2. Polar addition of the amine hydrosulfide to the olefin gives $C_6H_{11} \cdot SH$ which then reacts as expressed in (3) (i) and (ii):

$$Me \cdot CH_2 \cdot NH \cdot Et + 2S \longrightarrow H_2S + Me \cdot C(:S) \cdot NH \cdot Et \qquad (2)$$

$$C_6H_{10} + Et_2 \overset{(+)}{N}H_2 | \overset{(-)}{S}H \longrightarrow C_6H_{11}SH \begin{array}{l} (i) \quad C_6H_{11}SC_6H_{11} \\ \\ (ii) \quad C_6H_{11}S_2C_6H_{11} \end{array} \qquad (3)$$
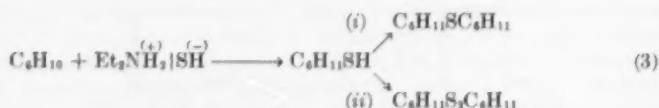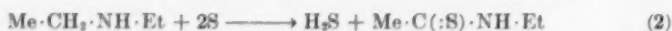
The polymeric material is formed by prior reaction of cyclohexene with sulfur to give cyclohexyl-cyclohexenyl sulfides[19] which then react with hydrogen sulfide and cyclohexanethiol as in Reaction 3.

Diethylamine and sulfur react with the trialkylethylenes to yield *tert.*-alkanethiols and di-*tert.*-alkyldisulfides as major products[29], thus confirming the polar nature of the reaction, with only minor amounts of the corresponding polysulfides and sulfurated polymers. Significantly, the monosulfide is absent and the degree of sulfuration is much lower than with cyclohexene, probably due to adverse steric factors impeding the additive powers of hydrogen sulfide and the intermediate *tert.*-alkanethiols.

This study of the influence of amines on olefin sulfuration is at present being extended to the amine sulfides, $R_2N \cdot S_x \cdot NR_2$, which have recently come into prominence as vulcanizing agents which impart reduced scorching and superior aging characteristics to furnace-black stocks[20,21]. It is already apparent that some of these compounds function in part at least by liberating hydrogen sulfide which then engages in additive crosslinking reactions.

The fully saturated and predominantly mono and disulfidic structures formed in the presence of amine contrast markedly with the apparent alkyl-alkenyl polysulfides obtained from mono-olefins in its absence[18,19]. Similarly, drastic constitutional differences occur in the products resulting from the sulfuration of trialkylethylenes[22], either (1) by the Peachey vulcanization process[33] involving the alternate treatment of the olefin with sulfur dioxide and hydrogen sulfide at 0°; or (2) with sulfur at room temperature in the presence

of zinc oxide, zinc di-*n*-butyldithiocarbamate, and a trace of hydrogen sulfide, a system simulating a low-temperature vulcanization recipe.   These processes result in *di-substitutive* crosslinking of the olefins, yielding di-alkenyltetrasulfides XIII.   It is a logical consequence that the similar sulfuration of the polyisoprenes, 2,6-dimethylocta-2,6-diene and squalene ($C_{30}H_{50}$) necessitates the experimentally observed absence of cyclic sulfides, which can result only from di-additive or substitutive-additive reactions.   A reasonable interpretation of the formation of XIII is that S_2 units (molecular or diradical) attack substitu-

$$\begin{array}{c} Me \\ | \\ R\cdot CH_2\cdot C:CH\cdot CH\cdot R' \\ | \\ S_4 \\ | \\ R\cdot CH_2C:CH\cdot CH\cdot R' \\ | \\ Me \end{array}$$

XIII
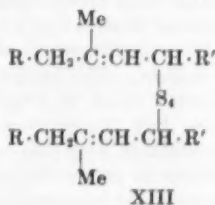
tively at α-methylenic groups followed by self-coupling of the alkenyldithio radicals $R\cdot CH_2\cdot C(Me):CH\cdot CH(R')\cdot S_2\cdot$, or the corresponding molecules $R\cdot CH_2\cdot C(Me):CH\cdot CH(R')\cdot S_2H$.

Significant differences in reaction path occur when these procedures are conducted at higher temperatures ($83°$ to $140°$ C)[22].   With the Peachey process, substitutive-additive crosslinking occurs and alkyl-alkenyl polysulfides result which resemble the products of olefin-sulfur interaction at $140°$ C. However, with the ultra accelerator system the reaction remains wholly disubstitutive, a feature undoubtedly connected with the function of zinc compounds in influencing the crosslinking reaction.

This function is clearly revealed by the fact that whereas reaction of 2,4-dimethylpent-2-ene with tetramethylthiuram disulfide alone at $140°$ C yields an alkyl-alkenyl polysulfide (average crosslink ca. S_4), in the presence of zinc oxide a mixture of dialkenyl-mono- and disulfides is obtained, indicative of exclusive di-substitutive crosslinking[22].   The composition of these products is inconsistent with the copolymerization mechanism of tetramethylthiuram disulfide vulcanization advanced by Craig et al.[24] involving the addition of S_2 units to the carbon-carbon double bonds.   Armstrong, Little, and Doak[17] determined analogous differences in the products of 2-methylbut-2-ene/sulfur interaction at $120°$ to $140°$ C in the absence and presence of zinc oxide, mercaptobenzothiazole, and zinc proprionate.   These authors contend that zinc mercaptides are intermediates, and therefore envisage coupling of RS— or RS$_x$— groups, or the corresponding mercapto compounds, as follows:

$$RH + S \longrightarrow RSH$$

$$2RSH + Zn^{(++)} \longrightarrow RS\!-\!Zn\!-\!SR \begin{array}{c} \nearrow RSR + ZnS \\ \\ \searrow \\ [8] \quad RSSR + ZnS \end{array}$$
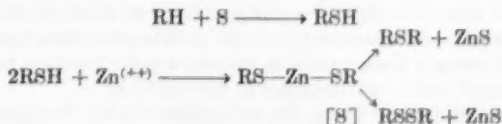
This mechanism finds support in (i) the linear relationship which exists between the degree of crosslinking (as measured by retractive force) and yield of zinc sulfide in mercaptobenzothiazole-accelerated vulcanizates produced under optimum crosslinking conditions (i.e., at $90°$ to $110°$ C and with high zinc salt

concentrations)[17,35,36]; (ii) the influence of zinc salts and various accelerator systems, especially diphenylguanidine, in favoring crosslinking over cyclization reactions in model systems[27]; and (iii) the greater retention of the original unsaturation in vulcanizates cured in the presence of zinc salts[27,35,39]. It cannot be generally valid, however, because of the lack of proportionality between the degree of crosslinking and yield of zinc sulfide at higher vulcanizing temperatures[36,40] and in mercaptobenzothiazole-accelerated vulcanizates deficient in zinc salt[40]. Adams and Johnson[40], who prefer to regard zinc sulfide formation as an index of degradative rather than crosslinking processes, explain this non-correspondence as due to thermal destruction of the crosslinks at the higher temperatures (138° to 149° C) with liberation of hydrogen sulfide which appears in the product as zinc sulfide. The higher crosslinking efficiency of an mercaptobenzothiazole-accelerated stock at lower temperatures[36] is in agreement with this interpretation, but the greater intrusion of di-substitutive coupling as compared with cyclization may also be important (cf. p. 403).

That zinc salts are not unique in promoting the coupling of RS_x-groups or RS_xH molecules at the expense of the competitive reactions has been demonstrated by Barton[41], who showed that numerous oxidizing agents act comparably.

To summarize, the combined action of temperature, zinc salts, and various accelerators influences the crosslinking efficiency of sulfur and the subsequent behavior of the vulcanizate by: (1) favoring the coupling of the intermediate RS_x-groups or RS_xH molecules which result from primary substitutive or additive reactions, and thereby inhibiting cyclic sulfide formation which characterizes a di-additive or substitutive-additive reaction sequence; and (2) reducing the number of sulfur atoms in the crosslink to the minimal value of 1–2 to give increased thermal stability. The high crosslinking efficiency which may be achieved by attention to both these factors is apparent from the work of Zapp et al.[42] Butyl-sulfur vulcanizates accelerated with tetramethylthiuram disulfide and tellurium diethyldithiocarbamate contain mono- and disulfide crosslinks and each crosslink formed requires only 1–2 combined sulfur atoms. This is a direct consequence of the negligible opportunity for intramolecular-sulfuration to compete with crosslinking in Butyl rubber which is devoid of the 1,5-diene system of polyisoprenes.

SUMMARY

Polyisoprenes react with sulfur both intramolecuarly and intermolecularly to yield cyclic sulfides and crosslinked sulfides, respectively. The structures of these have been examined for the reaction of the di-isoprene, 2,6-dimethylocta-2,6-diene, with sulfur at 140°. The cyclic sulfides consist of the two saturated compounds (I) and (II) and the two unsaturated compounds (III) and (IV). The crosslinked sulfide consists of a complex mixture in which unsaturated open chain and saturated and unsaturated cyclic sulfide structures have been identified. The structures of these products suggest a polar reaction mechanism, and also that hydrogen sulfide participates in the reaction.

The influence of organic bases, the sulfurizing agent, reaction temperature, and zinc salts on the nature of the sulfur linkage is discussed.

ACKNOWLEDGMENT

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SULFUR VULCANIZATION OF VINYL-SUBSTITUTED POLYSILOXANES *

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The principal method for crosslinking polysiloxane polymers to an elastic state has used peroxides such as benzoyl peroxide. The use of sulfur and accelerators as curing agents for silicone polymers was reported before a general professional group first in 1954[11]. The complexity of sulfur vulcanization is well known and the number of combinations of sulfur-accelerator-activators is almost infinite. It is therefore necessary to confine this discussion to relating the effects of sulfur-vulcanizing compounds more widely used in common sulfur-vulcanizable polymers such as natural rubber or GR-S.

A segment of a polysiloxane chain may be pictured schematically as follows
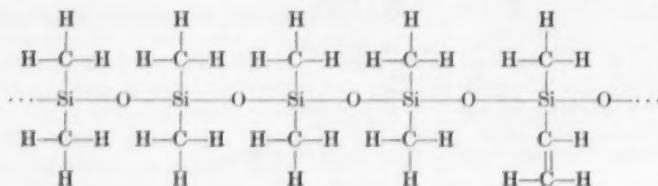
EXPERIMENTAL

The polymers used in this work were prepared by mixing the desired molar ratios of the cyclic tetramers of dimethylsiloxane (Me_2SiO) and methylvinylsiloxane (MeViSiO) and heating with potassium hydroxide as recommended by Hyde[9]. The properties of $(MeViSiO)_4$ were published[10] in 1955. The physical properties of $(MeViSiO)_4$ used in this work are: boiling point, 222° C at 760 mm.; n_D^{25}, 1.4325; d^{25}, 0.9828; viscosity, 3.48 centistokes at 25° C. All polymers were of comparable average molecular weight within the range of 449,000 to 571,000. The average molecular weights were calculated from intrinsic viscosity measurements using Barry's[1] formula,

$$[\eta] = 2 \times 10^{-4} M^{0.66}$$

A silica filler, Hi-Sil X303, and the vulcanizing agents were added to the polymers on a laboratory two-roll mill having roll diameters of 4 inches. Thirty parts by weight of silica based on 100 parts by weight of polymer were used in most of the sample stocks. Conventional rubber grade chemicals were used, with the exception of the metal oxides (zinc, lead, magnesium, calcium), zinc sulfide, and powdered zinc, which were reagent grade.

Each individual series of formulations was very carefully prepared using a base mix technique.   Curing agents were weighed on an analytical balance and added to portions of the base mix.   The resulting compounds were vulcanized within 24 hours after the base mix was prepared, to guard against possible irregularities due to the age of the mix.

The samples were vulcanized in a steam-heated press which had been preheated to the desired temperature.   The vulcanization time was measured from the instant of insertion of the sample in the press to the time when cooling was started by flushing the platens with cold water.   The cooling cycle required 19 seconds to cool from 160° to 100° C and a total of 40 seconds to cool below 50° C, as indicated by thermocouples embedded in the press platens.   The cooling times for vulcanization temperatures below 160° C were correspondingly shorter.   It was considered that very little additional vulcanization took place below 100° C and because the cooling cycle was short compared with the total vulcanization times used in these studies, the error introduced by the method used for the measurement of vulcanization time was negligible.   The test moldings were cut into tensile bars and tested on a Scott L-6 tensile testing machine according to ASTM designation D 412-51T.

There are several ways to evaluate the extent of vulcanization.   Swelling measurements, bound sulfur determinations, and modulus measurements are most commonly used.   Some of these methods can be combined to give a more detailed picture of the result of vulcanization.   For example, Zapp and others[14] did an excellent job of combining swelling measurements with organically bound sulfur content to determine the average number of sulfur atoms per crosslink. Tensile strength values may also be used to compare the relative extent of vulcanization, although the method is limited to the time region below the time required to develop the optimum tensile strength.   This is referred to as the interval of constructive vulcanization processes.   The drop in mechanical strength during the vulcanization process beyond the instant of optimum vulcanization is connected with an increase in crosslink density to a point at which orientation of the molecular chains becomes difficult.   Dogadkin and others[4] presented data which gave an excellent comparison of bound sulfur determinations, swelling measurements, and tensile strengths as a function of vulcanization time.   Their data substantiate the utility of tensile strength measurements as a means of following vulcanization rates within the previously mentioned limits.   Because of the ease of obtaining data, the tensile strength method for following vulcanization during the constructive vulcanization processes was chosen as the chief method used in this work to follow vulcanization.   Tensile strength was plotted as a function of vulcanization time for most of the curing recipes studied.

Values of the average molecular weight between crosslinks (M_c) for a number of unfilled samples were determined by swelling measurements.   The swelling measurements were carried out at $25° \pm 0.01°$ C using toluene as the solvent. A μ value of 0.465 as determined by Bueche[2] was used in conjunction with Flory's[5] equilibrium swelling relationship for calculating M_c.

VINYL GROUP CONCENTRATION

Polymers having 0.33, 1.00, and 4.00 mole per cent of methylvinylsiloxane units were compounded using 30 parts of silica, 2 parts of sulfur, and 0.5 part of Trimene base (aldehyde-amine) based on 100 parts of polymer, to determine the effect of varying the vinyl content (Figure 1).   The vulcanization time
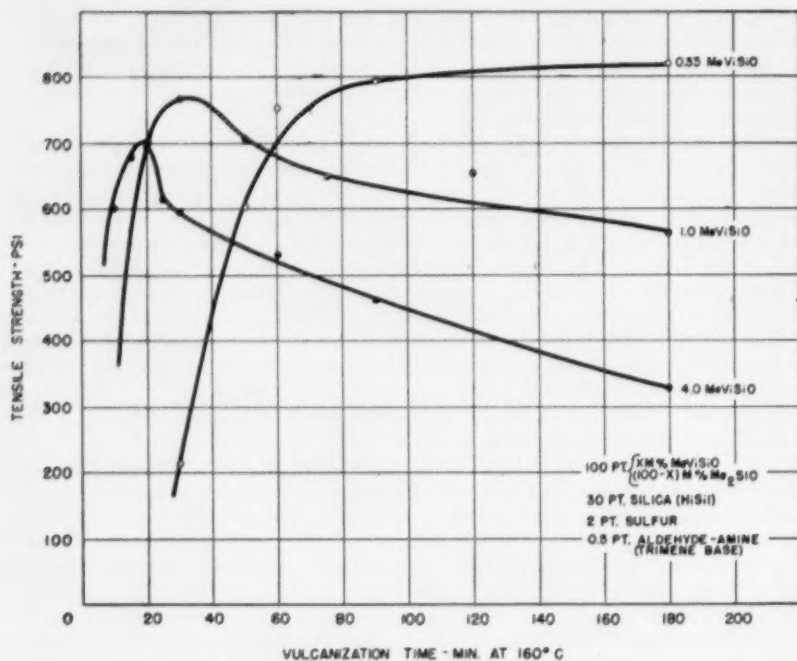
Fig. 1.—Effect of vinyl concentration on development of tensile strength.
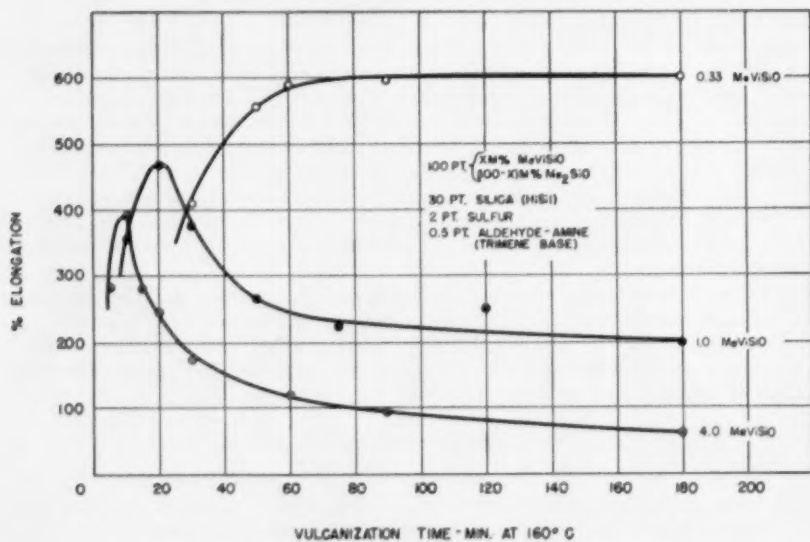
Fig. 2.—Relation of ultimate elongation to vinyl concentration.

varied inversely with approximately the 0.8 and 0.5 powers of vinyl concentra-
tion for vinyl content ranges of 0.33 to 1.0 and 1.0 to 4.0 mole per cent, respec-
tively.   The effect of vinyl content on the sharpness of the tensile strength peak
would suggest that the optimum average number of units between crosslinks
lies somewhere between 100 and 300 units, assuming that two vinyl groups are
involved in a crosslink.   Figure 2 gives the elongations for the same samples.
The elongations follow the expected trend of leveling off when the vinyl groups
have been utilized in the vulcanization process.   This same result was also
found for Butyl[13] with a low degree of unsaturation, and the limiting value
indicated by physical properties was verified by swelling measurements.   The
reciprocal of the elongations at the ultimate state of cure varies linearly with
the vinyl content.
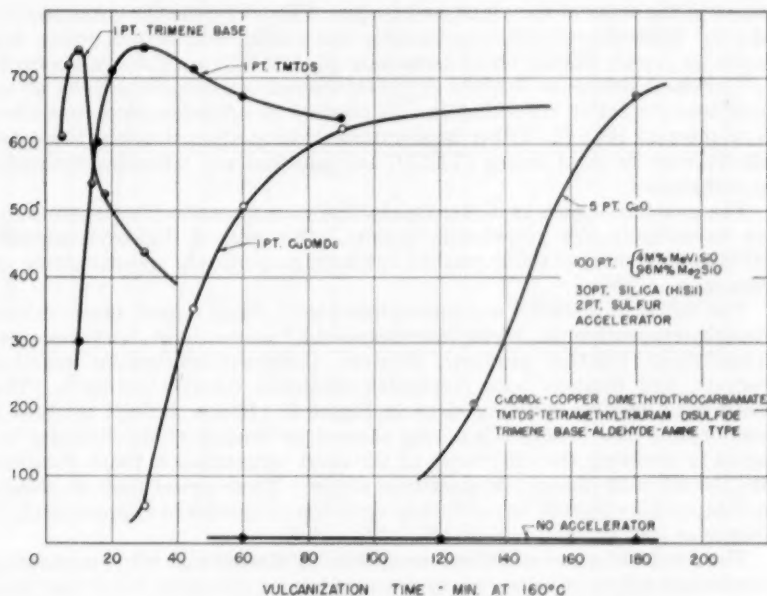
FIG. 3.—Relative activity of accelerators.

It is apparent from Figures 1 and 2 that the vinyl content of the polymer is a
determining factor in not only the combination of physical properties but also
the stability of the properties.   For example, a polysiloxane should have a
vinyl content of less than 1 mole per cent if it is to be subjected to temperatures
that will cause excessive crosslinking by means of sulfur vulcanization or oxida-
tion.

SULFUR–ACCELERATOR–ACTIVATOR COMBINATIONS

Polysiloxane polymers containing high concentrations of vinyl groups gave
poor vulcanizates with sulfur alone, and as the vinyl content was decreased, all
evidence of vulcanization disappeared.   Figure 3 shows the effect of a variety
of accelerators on sulfur vulcanization.   Two facts are apparent from this graph.

First, accelerators can make the difference between suitable vulcanization and no apparent vulcanization. Secondly, the specific accelerator plays an important part in determining the rate of vulcanization. The control for the series contained 2 parts of sulfur and after 180 minutes at 160° C showed no signs of vulcanization. The sample with 5 parts of calcium oxide in addition to the 2 parts of sulfur vulcanized in 180 minutes at 160° C to a fairly good rubber. A sample with 5 parts of zinc oxide showed no vulcanization after 200 minutes at 160° C, while 5 parts of lead oxide gave slight vulcanization after 180 minutes at 160° C. A sample with 5 parts of magnesium oxide developed optimum tensile strength in approximately 40 minutes at 160° C. This difference in activity of the metal oxides is probably due to their relative basicity.

The bivalent metal dithiocarbamates accelerate sulfur vulcanization of vinyl-containing polysiloxanes. The activity of these dithiocarbamates decreases in the order of zinc, lead, and copper. The difference in vulcanization rates for these dimethyldithiocarbamates was small. Out of this group, the results for copper dimethyldithiocarbamate (CuDMDC) are given in Figure 3.

Tetramethylthiuram disulfide (TMTD) showed considerable activity as an accelerator for sulfur vulcanization. It reached its optimum properties after 30 minutes at 160° C. Other accelerators showing approximately the same activity were its ethyl analog (TETD) and selenium and tellurium diethyldithiocarbamates.

The guanidines such as diphenylguanidine gave the second fastest acceleration to sulfur in this polysiloxane system. One part of diphenylguanidine (DPG) with 2 parts of sulfur reached optimum properties in approximately 10 minutes at 160° C.

The fastest acceleration was accomplished with strong organic bases such as tetraethylenepentamine, triethylenetetramine, Trimene base (diethylamine-formaldehyde reaction product), Beutene (butyraldehyde-aniline reaction product), and Heptene base (heptaldehyde-aniline reaction product). The results with Trimene base are given in Figure 3. It was difficult to classify these organic base compounds among themselves because of the difficulty involved in resolving the differences in the short vulcanization times obtained with the different compounds mentioned above. These strong basic accelerating compounds appeared to reach their optimum properties in approximately 7 minutes at 160° C.

The results of many additional compounding studies with vinyl-containing polysiloxane polymers using cure systems containing elemental sulfur may best be summarized by the following statements:

The amount of an accelerator such as Trimene base (aldehyde-amine type) is important in determining the vulcanization rate.

In general, zinc oxide and litharge retard vulcanization in this silicone system to varying degrees, depending on the type of acceleration used. For example, zinc oxide greatly retards the sulfur-diphenylguanidine system, but only slightly retards the sulfur-mercaptobenzothiazole (MBT) system.

Contrary to the action of zinc oxide and litharge, both magnesium oxide and calcium oxide slightly activate sulfur-accelerator cure systems.

In a TMTD-accelerated system the oxides of zinc and lead form their less active dithiocarbamates at the curing temperatures.

Organic acids such as stearic or benzoic acid retard and in many cases also inhibit vulcanization in this vinyl-containing polysiloxane system. In a sulfur-magnesium oxide accelerated system, the effect of organic acids was less severe than in a sulfur-TMTD-zinc oxide recipe.

Carbon black may be used as filler in sulfur-vulcanizable polysiloxanes. The alkaline furnace blacks give slightly faster vulcanization rates than a corresponding silica-filled stock. Acidic channel black-filled stocks give slower vulcanization rates than silica-filled stocks. Vulcanization of a carbon black-filled vinyl-containing polysiloxane is retarded by zinc oxide in much the same way as silica-filled stocks. The degree of retardation and inhibition exhibited by the presence of zinc oxide in carbon black-filled polysiloxanes depends also on the sulfur-accelerator combination. For example, the vulcanization of a furnace black-filled vinyl-containing polysiloxane is retarded less by zinc oxide in a sulfur-Santocure recipe than in a sulfur-TMTD recipe.
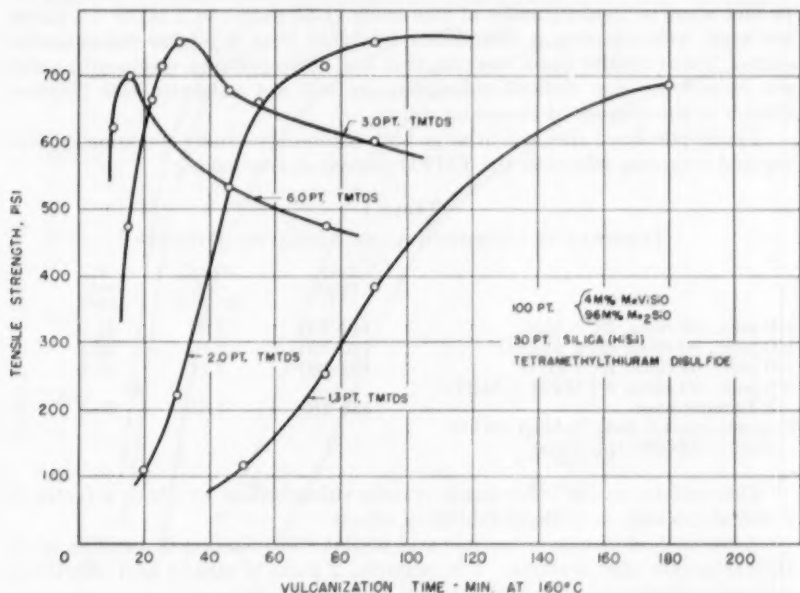
Fig. 4.—Effect of thiuram disulfide concentration in nonsulfur system.

NONELEMENTAL SULFUR–CURING SYSTEMS

Certain sulfur-containing accelerators are capable of crosslinking sulfur-vulcanizable organic polymers without the aid of elemental sulfur. Accelerators such as selenium or tellurium diethyldithiocarbamates and thiuram disulfides are of this type. These compounds are also capable of vulcanizing vinyl-containing polysiloxane stocks. Figure 4 shows the effect of different concentrations of TMTD on the rate of vulcanization. For concentrations of 3 parts of agent and below the vulcanization time varies inversely as the 2.3 power of the concentration.

The results of many additional compounding studies with vinyl-containing polysiloxane polymers using cure systems not containing elemental sulfur may best be summarized by the following statements:

Based on equivalent dithiocarbamate content, selenium diethyldithiocarbamate (SeDEDC) gives slightly faster vulcanization rates than TETD and

approximately four times the rate of tellurium diethyldithiocarbamate (Te-DEDC).

As anticipated, the bivalent metal dithiocarbamates such as copper, zinc, and lead dimethyldithiocarbamates are inactive as vulcanizing agents for this polymer system when used in the absence of elemental sulfur.

The effect of tetramethylthiuram monosulfide (TMTM) on TMTD recipes is to give tighter cures with very little change in the vulcanization rate. However, the tensile values are lowered from those of the control stock. This trend is different than for extracted pale crepe; Craig, Juve, and Davidson[2] found that TMTM both retarded and inhibited the TMTD cures.

Zinc oxide inhibits vulcanization of a TMTD or a similar type of cure system. In fact when equivalent moles of zinc oxide (1.35 parts) to TMTD (4 parts) are used, vulcanization is completely inhibited over a 5-hour vulcanization span. These results again suggest that the corresponding dithiocarbamates are formed, as zinc dialkyldithiocarbamate will not vulcanize this polymer system in the absence of elemental sulfur.

Finely powdered zinc and litharge both exhibit essentially the same inhibiting and retarding effects in the TMTD system as zinc oxide.

TABLE I

TEMPERATURE COEFFICIENTS AND ACTIVATION ENERGIES

Recipe	Temp. range, °C	Temp. coef. per 10° C	E, kcal./ mole
100 poly., 30 silica, 28, 5 MgO	140–160	2.54	31.5
100 poly., 30 silica, 28, 1 TMTD	130–160	2.15	26.4
100 poly., 30 silica, 28, 1 DPG	130–160	2.11	25.1
100 poly., 30 silica, 2 TMTD, 1 MBT, 3 Trimene base	130–160	1.85	20.3

Polymer was a 4 mole % MEViSiO-96 mole % Me₂SiO copolymer

Zinc sulfide, on the other hand, retards vulcanization by about a factor of 2 and shows only very slight inhibiting effects.

Acids such as stearic or benzoic acid inhibit vulcanization in disulfide or dithiocarbamate cure systems. For example, 2 parts of stearic acid effectively prevent suitable vulcanization with 3.0 parts of TMTD.

Mercaptobenzothiazole slightly retards and inhibits vulcanization in this elemental sulfur-free curing system.

Magnesium oxide, calcium oxide, and organic bases activate this elemental sulfur-free curing system.

TEMPERATURE COEFFICIENT OF RATE OF VULCANIZATION AND APPARENT ENERGY OF ACTIVATION FOR REACTION

The practical value of knowing the temperature coefficient of the rate of vulcanization is well known to the rubber technologist. The temperature coefficients for rubber were summarized from published data for 1930 to 1939 by Gerke[6]. The values ranged from 1.87-fold increase in rate per 10° C increase in temperature to 2.67, depending largely upon the accelerators used. These values, as given in the literature, are dependent to a small extent upon the method used to determine the values—i.e., bound sulfur or modulus measurements. It seemed worth while to study a variety of curing recipes in this vinyl-containing polysiloxane system. The methylvinylsiloxane content was kept

constant at 4 mole per cent throughout the different recipes, and the silica filler content was held constant at 30 parts by weight. The temperature coefficients and activation energies for the different systems are given in Table I.

Figure 5 shows the tensile strength values plotted as a function of vulcanization time at a series of temperatures for a curing system of 2 parts of sulfur-5 parts of magnesium oxide. Figure 6 shows a similar plot for a curing system of 2 parts of sulfur-1 part of TMTD. Figure 7 gives a plot of tensile strength vs time for a curing system of 2 parts of sulfur-1 part of diphenylguanidine. Figure 8 gives the curves of tensile strength vs time for a curing system of 2 parts of TMTD-1 part of MBT-3 parts of Trimene base.
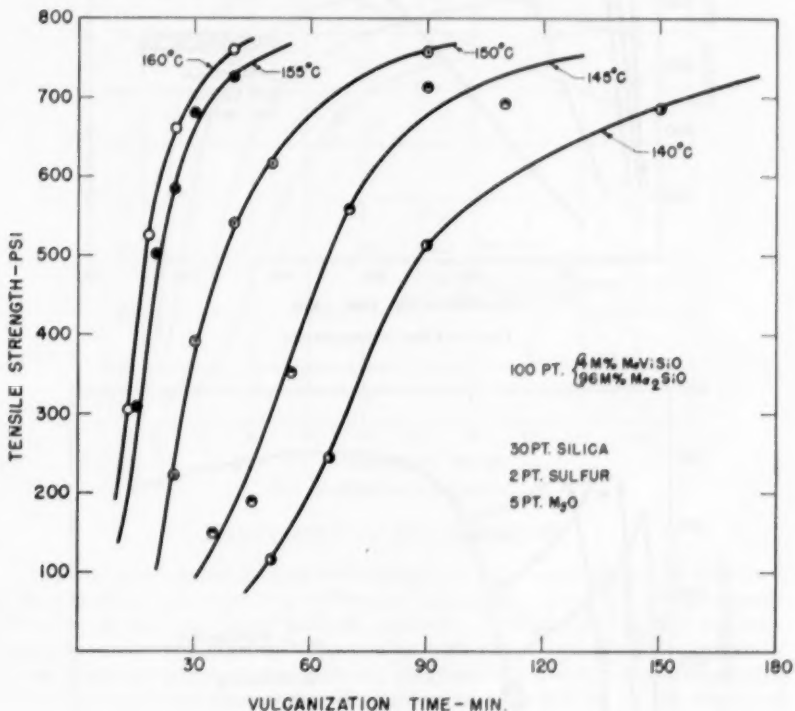
FIG. 5.—Effect of temperature.

The temperature coefficients for the rate of vulcanization in this polysiloxane system follow a very close parallel to organic rubber values. For example, a rubber-sulfur system is usually quoted[6] as having a temperature coefficient of around 2.5 as compared with 2.54 for the sulfur-magnesium oxide combination in this system. The temperature coefficient values of TMTD in rubber[6] and in this polymer system are practically identical.

The Arrhenius activation energy values (E in kilocalories per mole) calculated from these data are very close to values found in the literature for sulfur vulcanization of organic polymers. For the sulfur-magnesium oxide system a value of 31.5 kcal. was found. This value is in the expected range for heat of
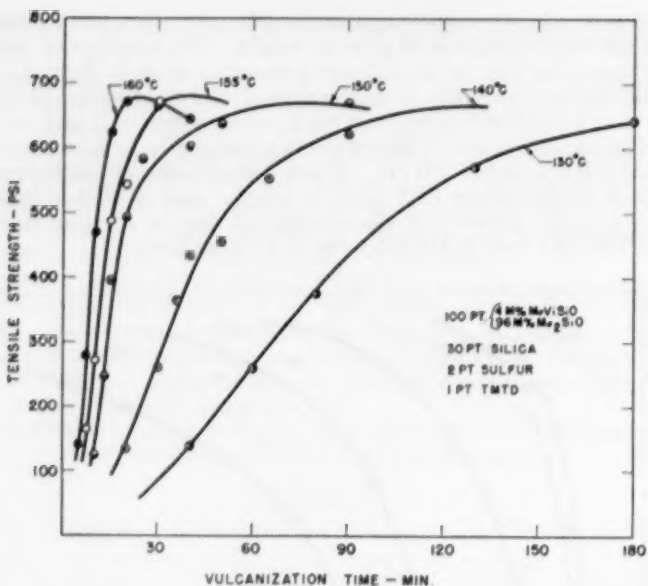
Fig. 6.—Effect of temperature.
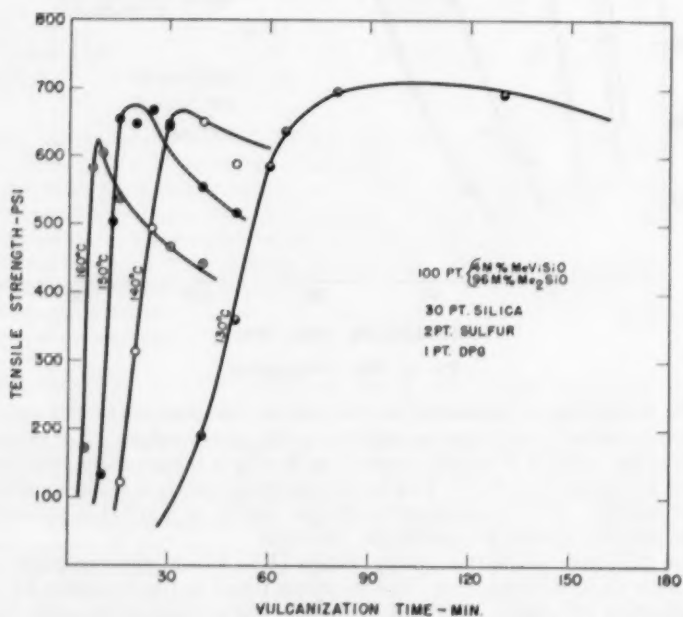
Fig. 7.—Effect of temperature.

reaction of sulfur, which was calculated by Powell and Eyring[12] to be 27.5 ± 5 kcal.   Gordon[7] determined a value for unaccelerated Buna vulcanization to be 30.5 to 35.0 kcal. and 23.0 kcal. for Butyl[8] accelerated by tellurium diethyldithio-carbamate.   Dogadkin and coworkers[4] obtained 31.5 kcal. for sulfur-zinc oxide-stearic acid combination in smoked sheet and from 22.9 to 24.5 kcal. for various accelerator combinations in the same system.   Thus the values for activation energies for the various accelerator combinations in this vinyl-containing poly-siloxane system seem in line with the values quoted in the literature for other polymers.
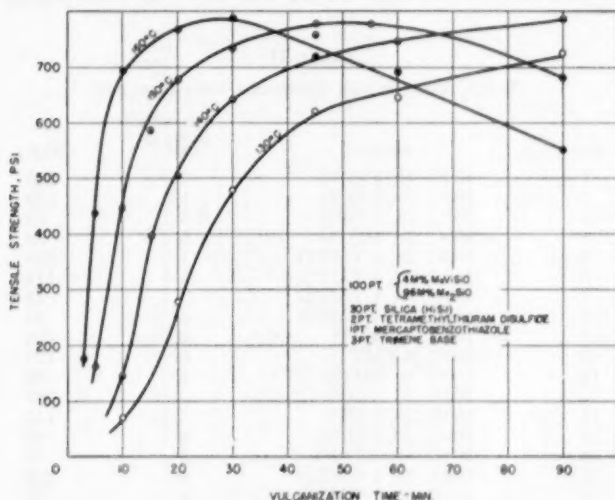
FIG. 8.—Effect of temperature.

VINYL GROUPS IN CROSSLINKS

It seemed of interest to gain some insight as to the role played by the vinyl groups in sulfur vulcanization of these polysiloxanes.   As in the case of organic polymers, it was established that the presence of unsaturated groups was nec-essary to render the polymer vulcanizable with sulfur and related compounds. It was found qualitatively by following progressive times of vulcanization with infrared curves that the number of vinyl groups diminished as the degree of crosslinking increased.   This indicated that the vinyl groups were probably a part of each crosslink.

As an all-methyl substituted polysiloxane did not show evidence of vulcani-zation with sulfur under normal vulcanization temperatures, it seemed likely that methyl groups would not be involved in crosslinks in the vinyl-substituted polysiloxane.   This would mean that the most probable crosslink would include two vinyl groups joined with sulfur.   This conjecture would be strengthened by determining the $(D.P.)_c$ values (the average number of R_2SiO units between points of crosslinking) for a range of vinyl-content polymers.   For example, if two vinyl groups are involved per crosslink, polymers having molar contents of 0.5, 1.0, 2.0, and 4.0 per cent would have $(D.P.)_c$ values of 200, 100, 50, and 25, respectively.   Furthermore, if one vinyl group is involved per crosslink, the

corresponding (D.P.)$_c$ values would then be 100, 50, 25 and 12.5. The above conjecture was tested by a series of experiments. First, a copolymer 2.0 M% MeViSiO–98.0 M per cent Me$_2$SiO, was compounded with 2 parts of sulfur-1 part of diphenylguanidine combination and 2 parts of sulfur-1 part of TMTD combination to determine the vulcanization time at 160° C necessary to reach the respective ultimate states of cure. The results are given in Table II. Three hours at 160° C was considered adequate for the polymer-sulfur-diphenylguanidine system and 6 hours at 160° C was necessary for the polymer-sulfur-TMTD system to reach ultimate states of cure. These vulcanization' times were then used for subsequent work with copolymers containing 0.5, 1.0,

TABLE II

(D.P.)$_c$ VALUES FOR UNFILLED VULCANIZATES

No.	Recipe[a]	Vulc. time, hours at 160° C	(D.P.)$_c$
1	100C, 2S, 1 DPG	1	246
2	100C, 2S, 1 DPG	1.5	139
3	100C, 2S, 1 DPG	3	63
4	100C, 2S, 1 DPG	6	59
5	100C, 2S, 1 TMTD	1	224
6	100C, 2S, 1 TMTD	1.5	112
7	100C, 2S, 1 TMTD	3	75
8	100C, 2S, 1 TMTD	6	63
9	100C, 4 TMTD	6	258
10	100C, 6 TMTD	6	121
11	100C, 10 TMTD	6	69
12	100A, 2S, 1 DPG	3	262
13	100B, 2S, 1 DPG	3	115
14	100C, 2S, 1 DPG	3	63
15	100D, 4S, 1 DPG	3	32
16	100A, 2S, 1 TMTD	6	232
17	100B, 2S, 1 TMTD	6	93
18	100C, 2S, 1 TMTD	6	63
19	100D, 4S, 1 TMTD	6	34
20	100A, 2S, 5 MgO	6	668
21	100B, 2S, 5 MgO	6	183
22	100C, 2S, 5 MgO	6	107
23	100D, 4S, 5 MgO	6	52

[a] A. Copolymer-0.5 mole % MeViSiO-99.5 mole % Me$_2$SiO.
B. Copolymer-1.0 mole % MeViSiO-99.0 mole % Me$_2$SiO.
C. Copolymer-2.0 mole % MeViSiO-98.0 mole % Me$_2$SiO.
D. Copolymer-4.0 mole % MeViSiO-96.0 mole % Me$_2$SiO.

2.0, and 4 mole per cent MeViSiO and 99.5, 99.0, 98.0, and 96.0 mole per cent Me$_2$SiO, respectively. To each of these copolymers were added 1 part of either DPG or TMTD and 2 parts of sulfur, with the exception of the 4 mole per cent MeViSiO-containing copolymers, to which 4 parts of sulfur were added. Another series was also evaluated having 5 parts of magnesium oxide as the accelerator along with the sulfur concentrations mentioned above.

Data given in Table II and plotted in Figure 9 show how the experimental (D.P.)$_c$ values compare with the theoretical curve, which assumed that two vinyl groups would be involved in each crosslink. The results give good evidence that the above conjecture is correct. It is interesting to compare the similar results of the DPG- and the TMTD-accelerated stocks with the results of the magnesium oxide-accelerated stocks. It would appear that fewer vinyl

groups are destructively blocked as crosslink sites in the cases of DPG and TMTD than in the case of magnesium oxide.

SUMMARY

The vinyl content of the polysiloxane polymer affects the rate of vulcanization in such a way that the vulcanization time varies inversely with the vinyl concentration raised to a power less than 1. Furthermore, this power appears to be dependent upon the vinyl concentration, so that a stationary value cannot be quoted.
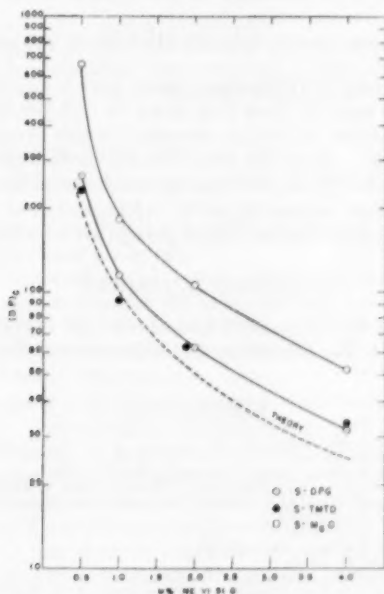
Fig. 9.—Relation of $(D.P.)_c$ to vinyl content.

For recipes containing elemental sulfur, several conclusions may be made :

Sulfur alone crosslinks only polysiloxane polymers of high vinyl content. A 4 mole per cent vinyl-containing polymer exhibited no vulcanization after 3 hours at 160° C with sulfur alone.

Vulcanization times in the same range as those found with sulfur-vulcanizing organic polymers were obtained in this polysiloxane system by the proper choice of accelerators.

Starting with the most active, compounds for accelerating or activating this vinyl-containing polysiloxane-sulfur system were: strong organic bases (TEPA), DPG, thiuram disulfides (TMTD), magnesium oxide, bivalent metal dithiocarbamates, thiazoles (MBT), weak organic bases (aniline), calcium oxide.

Zinc oxide and litharge are inhibitors in this system to varying extents, depending on the accelerator present.

Organic acids such as stearic acid inhibit vulcanization in this system.

For recipes void of elemental sulfur, the following conclusions may be made:

Accelerators that vulcanize vinyl-containing polysiloxanes without the aid of elemental sulfur follow very closely the list of compounds capable of vulcanizing organic polymers.

Vulcanization time is dependent upon the concentration of accelerator.

Zinc oxide, powdered zinc, lead oxide, and organic acids all gave marked retarding and inhibiting effects on systems using agents, such as TMTD or SeDEDC.

Zinc sulfide showed only slight retarding and inhibiting effects.

Magnesium oxide is an activator in this system as in the elemental sulfur system.

Strong organic bases greatly increase the rate of vulcanization.

This vinyl-containing polysiloxane system gave temperature coefficients for rate of vulcanization ranging from 2.54 down to 1.85 per 10° C change in temperature. The Arrhenius activation energies for this system ranged from 31.5 to 20.3 kcal. per mole. Both the temperature coefficients and the activation energy values depended upon the type of accelerators present. Both agreed very well with literature values for sulfur vulcanization of organic polymers.

$(D.P.)_c$ data indicated that two vinyl groups are involved in each cross link.

ACKNOWLEDGMENT

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DISULFIDE INTERCHANGE IN POLYSULFIDE POLYMERS *

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INTRODUCTION

At the time this investigation was initiated (1944) there was no general recognition of the occurrence of a disulfide/disulfide or disulfide/thiol interchange reaction:

$$RSSR + R'SSR' \rightleftharpoons 2RSSR'$$
$$RSSR + R'SH \rightleftharpoons RSSR' + RSH$$
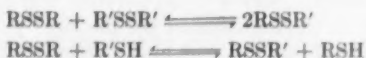
An experimental program studying polysulfide polymers produced conclusive evidence that these reactions did occur.

A literature search revealed that, with few exceptions, reactions between thiols and disulfides were treated as oxidation reduction reactions even though the early work of Lecher[1] had shown an exchange reaction to occur. Later work in the field which has provided unequivocal proof of redistribution phenomena is reviewed later in this paper.

Polysulfide elastomers were found to be a convenient tool for studying disulfide interchange. The viscosity of a polymer is profoundly affected by its molecular weight. Scission of a polymeric disulfide by a simple disulfide or thiol lowers the molecular weight and thus proves to be a sensitive method for detecting the occurrence and extent of disulfide interchange.

This work deals with a study of disulfide/disulfide and disulfide/thiol interactions, as well as the use of these reactions to modify polysulfide polymers. This work has been cited by others[2] but has not been published by us until now.

EXPERIMENTAL METHODS

Polymer preparation.—Water dispersions of polysulfide polymers were prepared from organic dihalides in a five-liter, three-necked flask equipped with stirrer, reflux condenser, dropping funnel, and thermometer. The sodium disulfide solution (4.80 moles), approximately two molar in concentration, was placed in the flask. To the agitated solution was added a wetting agent (1.0 g. of Nekal BX) and sodium hydroxide (0.32 mole), followed by dropwise addition of a 25 per cent solution of magnesium chloride (0.16 mole) to form magnesium hydroxide.

The contents of the flask were heated to 93° C and then the desired dihalide (4.0 moles) was added slowly over a one-hour period. External heating or cooling, as necessary, was applied to keep the contents of the flask between 90 and 95° C. At the end of the one-hour addition, the reaction mixture was heated to 100° C and kept at that temperature for one hour. After filling the flask

with cold water, the stirring was discontinued and the polymer dispersion was allowed to settle.

Washing the polymer free of excess sodium polysulfide and sodium chloride produced in the reaction was accomplished by siphoning off the supernatant liquid and refilling the flask with hot (70° C) water. This operation was carried out repeatedly until the supernatant liquid no longer caused discoloration of lead acetate paper.

Polymer treatment.—Treatment of a polymer with the various chemical reagents employed was carried out in a beaker equipped for heating and agitation. One mole of the polymer based on the segment weight was placed in the beaker as a water dispersion of 30 per cent solids content. The agitated water dispersion was heated to 70° C and the desired chemical reagents were added. Heating was continued for 30 minutes. The contents of the beaker were then poured into an equal volume of water and the polymer dispersion was washed by successive decantations.

Cake preparation.—A solid cake of dried polymer was prepared for examination and measurement of the hardness of the modified polymer. A quantity of the aqueous dispersion of polymer was filtered through filter paper held in a small Büchner funnel mounted in a suction flask connected to a water aspirator. Sufficient dispersion was used to build up a wet cake of at least ¾ inch in thickness. Care was needed to remove as much water as possible but yet to break the vacuum connection before cracks develop on the surface of the cake. The cake, still on the filter paper, was removed and dried in an oven at 70° C for 24 hours. The durometer hardness (Shore A) was then measured.

EXPERIMENTAL RESULTS

Effect of butyl chloride during polymerization.—Three polysulfide reactions were run using a ratio of 0.95 mole of dichloroethyl formal to 0.05 mole of butyl chloride. In the first reaction the dihalide and monohalide were mixed before addition to the sodium disulfide solution. In the second reaction the butyl chloride was added to the aqueous sodium disulfide solution and allowed to react completely before the dichloroethyl formal was added. In the third reaction the order was reversed so that the dichloroethyl formal was allowed to react before the butyl chloride was added.

Under these reaction conditions, dichloroethyl formal used alone reacts with aqueous sodim disulfide to form a soft elastomer. Butyl chloride reacts with aqueous sodium disulfide to form butyl disulfide. With a mixture of 0.95 mole of dihalide to 0.05 mole of monohalide, the reaction product should be a low molecular polymer with an average chain length of 40 units (38 segments plus 2 terminals).

The three polymerization reactions described all produced identical viscous liquid polymers. This experiment strongly indicates that, in the presence of sodium polysulfide, a redistribution occurs between butyl disulfide and the disulfide polymer from dichloroethyl formal to produce the same low polymer formed from the mixed halides.

Effect of butyl derivatives after polymerization.—In order to clarify the results of the previous experiment, the effect of butyl chloride, disulfide, mercaptan, and sulfide was tried on a preformed disulfide polymer of dichloroethyl formal. The reagents were added, as described in the Experimental Methods section, to the aqueous dispersion of high molecular disulfide polymer. A ratio of 0.05 mole of butyl groups per 1.0 mole of polymer based on the segment weight was

used. All reagents were tried in the presence and absence of 0.10 mole of sodium disulfide.

The results of the experiment summarized in Table I show that butyl chloride, disulfide, and mercaptan in the presence of sodium disulfide have a profound effect upon lowering the molecular weight of a polymer containing disulfide links. All of the three materials exist as or can be converted to butyl disulfide when sodium disulfide is present. One common reaction is therefore the reaction of butyl disulfide with a polymer of high molecular weight to form a low molecular liquid polymer with butyl groups as terminals. Otto and Rossing[2] have shown that sodium sulfide can convert disulfides to mercaptides so that in this manner butyl disulfide can be converted, at least in part, to the sodium salt of butyl mercaptan. Butyl mercaptan has been shown to react with the polymer even in the absence of sodium disulfide so that the mercaptan itself may be the essential form needed rather than the disulfide.

Copolymerization by interchange.—Polysulfide polymers have been often prepared as copolymers by using a mixture of dihalides instead of a single dihalide. The results obtained with butyl disulfide showed that it should be possible to prepare a true copolymer by heating together two different polysulfide polymers in the presence of sodium disulfide.

TABLE I

EFFECT OF BUTYL DERIVATIVES UPON POLYSULFIDE POLYMERS

| | Product | |
Additive	Na_2S_2 absent	Na_2S_2 present
None	Rubber	Rubber
Butyl chloride	Rubber	Liquid
Butyl disulfide	Rubber	Liquid
Butyl mercaptan	Liquid	Liquid
Butyl sulfide	Rubber	Rubber

Two polymers were selected such that they would be mutually incompatible: ethylene disulfide polymer ($-CH_2CH_2SS-$)$_n$, which is a hard plastic material, and triglycol disulfide ($-CH_2CH_2OCH_2CH_2OCH_2CH_2SS-$) polymerized in the presence of 5 mole per cent butyl chloride so that it was a viscous liquid. Water dispersions of the two polymers were blended so as to contain equal amounts of the two polymeric structures. One such mixture was heated 60 minutes at 90° C and another heated similarly after adding sodium disulfide. After washing and drying in an oven at 70° C the mixture heated in the absence of sodium disulfide yielded an inhomogeneous mixture of fine particles of the ethylene disulfide suspended in the viscous triglycol liquid polymer. The mixture heated in the presence of sodium disulfide gave a homogeneous liquid polymer of significantly higher viscosity than the triglycol disulfide.

One mole (based on segment weight) of a water dispersion of the disulfide polymer from bis(2-chloroethyl) formal was treated with 0.05 mole of bis(2-mercaptoethyl) formal, followed by acid coagulation and drying. As a result of this treatment, the rubber of high molecular weight had been converted to a very viscous liquid. The terminals should be thiol groups. This was confirmed by oxidation of the viscous liquid back to the high polymer using lead peroxide. The liquid polymers resembled in every way the liquid polymers with terminal thiol groups made by reduction of disulfide groups by sodium hydrosulfide and sodium sulfite described in an earlier publication[4]. If 0.25 mole of sodium disulfide is added to the water dispersion either after or during

the treatment with dithiol, the product after drying is a rubber of high molecular weight.

True polysulfide copolymers can thus be readily prepared from two different polymers by heating together a mixed water dispersion in the presence of sodium disulfide or by treatment of a water dispersion with a dithiol followed by oxidation or sodium disulfide treatment. This method of preparing copolymers is often exceedingly convenient when a number of copolymers of varying compositions is wanted.

It has been established by the previous experiments that disulfide interact or redistribute in the presence of aqueous sodium disulfide. Although the mechanism of interchange is not definitely known, there are a number of conclusions that can be drawn: (1) The disulfide links in a polymer must be constantly rearranging so there is no basic integrity in any disulfide link. This situation resembles that present in polyesters under conditions such that ester interchange takes place. The molecular weight distribution curve in polysulfides should theoretically be the same as that found by Flory for polyesters[5] as a consequence of random interchange. (2) Varying reactivity of the halide groups in different dihalide monomers would not be expected to influence the sequence of the segments in the copolymer chains. Even if one dihalide reacted with the sodium disulfide completely before the other dihalide started, redistribution of disulfide links would give a random arrangement in the final copolymer.

Effect of polymer washing.—In the preparation of a polysulfide polymer the water dispersion is customarily washed free of soluble salts, including the excess of sodium polysulfide used, before any examination of the polymer is made. To examine the state of the polymer in the presence of the sodium polysulfide, a quantity of freshly polymerized latex was poured into a Büchner funnel and a cake prepared. A portion of the water dispersion of the same polymer was washed clean as usual and a cake prepared. The cake from the washed polymer was a tough rubber whereas the cake from the unwashed portion was a soft gum. Washing the gum by kneading it in running water made it tough and rubbery. This experiment conforms with the view that sodium disulfide can convert some disulfide groups to mercaptans or mercaptides[4]. The action is reversible and recombination takes place during the normal washing operation after the polymerization.

Crosslinking.—A series of disulfide polymers was prepared from dichloroethyl formal (98 per cent) and 1,2,3-trichloropropane (2 per cent) by two different methods. In the first reaction a mixed halide feed was used. In the second, the dichloroethyl formal alone was used in the reaction. The polymeric latex was washed and then treated with the trichloropropane and a small amount of sodium disulfide (0.10 mole/mole of polymer segments) to effect disulfide interchange.

The two rubbers produced were compounded and vulcanized with lead peroxide[6]. They had equivalent resistance to compression set at 70° C by ASTM D-395-49T Method B. This shows that both methods of preparing the polymer produced a crosslinked structure. A rubber prepared by the same procedure without trichloropropane has no resistance whatsoever to compression set at elevated temperatures.

Introduction of termina's.—Redistribution techniques provide a convenient method of preparing polysulfide polymers in any desired molecular weight range with various functional groups as terminals[7]. Treatment of a water dispersion of polymer with (1) a simple organic disulfide and small quantities of sodium

disulfide or (2) a thiol followed by an oxidation step produces such materials. The functional group on the simple disulfide or thiol is transferred to the end of the polymer chain. The molecular weight of the product is controlled by the mole ratio of simple disulfide or thiol to the polymeric disulfide:

$$—SS— + HOCH_2CH_2SSCH_2CH_2OH \longrightarrow —SSCH_2CH_2OH + HOCH_2CH_2SS—$$
$$—SS— + NH_2CH_2CH_2SH \longrightarrow —SSCH_2CH_2NH_2 + HS—$$
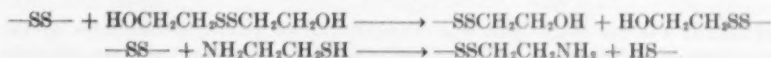
The treatment of the polymer with thiol, followed by oxidation, allows the insertion of terminal groups such as nitrile or aldehyde which are not stable to sodium polysulfide.

DISCUSSION

The experimental results presented conclusively showed the ready interchange of disulfide groups in the presence of sodium disulfide. They also showed that sodium disulfide was not needed if thiol groups were present and thereby suggested that this might be the mechanism of disulfide interchange. The interactions between thiol and disulfide groups have been of great interest especially in the biochemical field. Investigators of proteins, wool, and hair have all been concerned with this reaction. Most of them have worked with the cystine combined in a polypeptide chain. It should be noted that cystine is a particularly active disulfide and undergoes reaction more readily than simple aliphatic disulfides.

Lecher[1] in 1920 had reported that the sodium salt of thiophenol reacted with the unsymmetrical disulfide o-nitrodiphenyl disulfide to yield as main products diphenyl disulfide and the sodium salt of σ-nitrothiophenol. Lecher explained the results by postulating reduction of a disulfide by the salt of the thiol in a similar manner to the known reduction by alkali sulfides[2].

$$R'—S—S—R' + 2KSK \longrightarrow 2R'SK + KSSK$$
$$R'—S—S—R' + 2RSK \longrightarrow RSSR + 2R'SK$$

Goddard and Michaelis[3] found that thiols such as thioglycolic acid could be used to convert the combined cystine in keratin to combined cysteine. This reagent has since been used widely in studies with wool and other cystine-containing proteins to effect reduction. The thiol is used usually in large excess so that all of the combined cystine is converted to combined cysteine. Either a reduction or an interchange mechanism would produce this same effect under these circumstances. In one case, formation of a mixed disulfide between the polypeptide and the thioglycolic acid was noted[9]. Toennies[10] had also concluded that a reversible equilibrium existed between the cystine and thiourea to form cysteine and the unsymmetrical disulfide, S-(guanylthio) cysteine. Formulating thiourea as the zwitter ion:

$$Cys—SS—Cys + \underset{\underset{NH_2^+}{|}}{\overset{\overset{H_2N}{|}}{C}}—S^- + HCl \rightleftharpoons Cys—S—S—\underset{\underset{\underset{Cl^-}{NH_2}}{|}}{\overset{\overset{NH_2}{|}}{C}} + Cys—SH$$
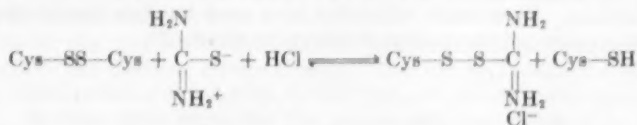
Kassell and Brand[11] also explicitly stated that disulfide/thiol interchange probably occurred in the cystine system.

Bersin and Steudel[12] studied the equilibrium involved in the thiol/disulfide system. They discussed the possibility of an unsymmetrical disulfide being

the primary reaction product between *l*-cystine and thioglycolic acid. They concluded that the mixed disulfide was formed by the reaction:

$$RS^- + R'SSR' \longrightarrow R'S^- + R'SSR$$

but that it was not stable and was converted to symmetrical disulfides by the same type of reaction. Alkalinity had a pronounced effect on increasing the rate of reaction[12,13].

Stern and Tobolsky[14], in a study of the stress relaxation of polysulfide rubbers, stated that disulfide interchange would account for the results obtained. In a later study, Mochulsky and Tobolsky[2] diffused butyl mercaptan into the disulfide polymers and studied the effect on stress relaxation.   The acceleration was so pronounced that they concluded that trace amounts of thiol groups in the disulfide polymer alone could account for the observed relaxation.   These low concentrations of thiol groups could well be present because of nonquantitative oxidation of thiol to disulfide groups in the vulcanization of the rubber. Ultraviolet irradiation was also found to have a pronounced effect on accelerating stress relaxation confirming the views of the authors that the relaxation phenomena were chemical rather than physical.

Gorin, Dougherty, and Tobolsky[15] continued their studies by examining the reaction of propyl disulfide with decyl mercaptan.   The reaction was surprisingly slow even at 140° C.   Kleiman, in a series of patents, claimed that alkali metal salts of thiols[16], halogens and halogen halides[17], and organic peroxides[18] would all catalyze the reaction of disulfide with thiol and also disulfide with disulfide.   It was also claimed that heat[19] or light[20] alone would cause reaction.

The reaction between a symmetrical disulfide and a thiol has been used for the production of unsymmetrical disulfides[21,22] in the presence of an alcoholic solution of alkali.   It was found that the reaction of an aliphatic mercaptan and an aliphatic disulfide in the absence of solvent occurred in the presence of light[22].   These authors and others[23] confirmed this effect by showing that polymerization of vinyl monomers was caused by disulfides when irradiated to presumably form sulfenyl radicals.   The redistribution of unsymmetrical aromatic disulfides was also found to occur under the influence of light[24].   It has been claimed, also, that two symmetrical disulfides can be caused to redistribute to produce unsymmetrical disulfides[25] by treatment with alkali sulfide and alkali in the presence of a hydroxyl-containing solvent.   The reverse reaction has been claimed to occur[26] in the presence of an alkanolamine solvent.

Cyclic disulfides can be converted to polymeric disulfides by trace amounts of sodium polysulfide[27] or sodium salts of thiols[28] and by irradiation with ultraviolet light[22,29].   A cleavage of the disulfide group to form a sulfenyl radical is probably the initiating process followed by reaction of the radical with more cyclic disulfide.   Even water which has been postulated to cleave disulfides[30] will in time cause polymerization of the cyclic disulfide[27].
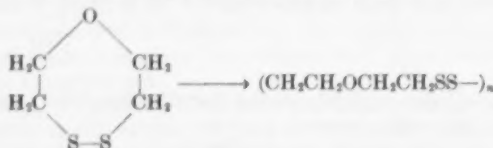
The interest in the thiol/disulfide relationship had continued in the biochemical field. Huggins, Tapley, and Jensen[31] used the work of Tobolsky as a basis for concluding that the thiol/disulfide reaction accounted for the necessity of thiol groups in the denaturation of certain proteins by urea. Sanger[32] prepared and isolated the mixed disulfide from cystine and bis-2,4-dinitrophenyl-cystine using hydrochloric acid as a reaction medium. The mixed disulfide of cysteine and penicillamine was also prepared by an interchange reaction[33]. Mixed disulfides were also prepared by the exchange of an aromatic disulfide with the thiol groups present in tissue proteins[34].

It was concluded that the denaturation of ovalbumin[35,36] and bovine plasma albumin[37] was due to the formation of disulfide crosslinks. These disulfide crosslinks were presumed to occur by the interaction of a thiol group in one molecule with an intramolecular disulfide link in another. Two protein molecules were thus linked together by a disulfide linkage with a free thiol group available for continuing the reaction.

Recently, Whitman and Eckstrom[38] discussed the applicability of the concept of interchange to the cold waving of hair. They stressed in particular the influence on the equilibrium of the immobility of the disulfide and thiol groups in the combined cystine and cysteine. Rosenthal and Oster[29] also treated this same stereochemical effect and discussed in detail the structure of cystine and the resultant effect on the reactivity of the disulfide bond. Using mesocystine as the disulfide they have been able to use the rotation of polarized light to measure accurately thiol/disulfide interchange[40].

Radioactive sulfur atoms have been recently used as tracers to give useful information on interchange phenomena. Fava and Iliceto[41] showed that interchange between butyl mercaptan and dibutyl disulfide was negligible in absolute ethanol. The reaction was measurably faster in aqueous alcohol and extremely rapid if the thiol was used in the form of the sodium salt. Guryanova and Vasileva[42] confirmed with similar methods that ultraviolet light promoted exchange between disulfides and thiols[22].

The interchange of disulfide groups can evidently occur through two distinct types of cleavage of the disulfide link: (1) a homolytic fission promoted by radiation to form two sulfenyl radicals presumably short lived[42], and (2) an ionic fission promoted by chemical reagents which produce at least one sulfenyl ion (RS^-). These reactions may be regarded as the initiation process. The propagation of the reaction is probably an ionic or radical displacement of sulfenyl ions or radicals on an intact disulfide group.

The interchange in polysulfide polymers described here most likely is an example of the ionic mechanism. The pH of the water dispersions is above 8 due to the magnesium hydroxide present as a nucleating agent. It has been shown that an alkaline environment promotes the interchange[12,12]. It should be noted that cystine, which is active in exchange, has a basic group already present in the molecule.

Whatever the mechanism, the resultant equilibrium must be influenced by the nature of the disulfide groups present. For linear aliphatic disulfides the random distribution of 1:2:1 with the unsymmetrical one predominating was found[21]. In some cases where the two groups are quite different the unsymmetrical disulfide is preferentially formed. More information is needed on the effect of disulfide structure and the effect of reagents on disulfide cleavage before the mechanism of disulfide interchange is clarified.

SYNOPSIS

A study has been made on the effect of thiols and disulfides on lowering the molecular weight of polysulfide polymers. It was shown that in the presence of aqueous sodium disulfide there is an interchange of chain segments. This effect is observable if a simple organic disulfide is present in the system, resulting in a lower molecular weight. Copolymers can be prepared by heating together in the presence of sodium disulfide, aqueous dispersions of two different polysulfide polymers. When thiols are present in the system, interchange of disulfide groups occurs in the absence of sodium disulfide. The results show that disulfide/disulfide redistribution and thiol/disulfide interchange take place in polysulfide polymers. The occurrence of these same reactions has recently been recognized by workers in the biochemical field. A literature survey of thiol/disulfide reactions showed that results formerly attributed to oxidation reduction reactions could be also explained by an interchange mechanism.

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STRESS RELAXATION STUDIES OF THE VISCOELASTIC PROPERTIES OF POLYMERS *

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An ideally elastic substance subjected to simple tension obeys Hooke's law in the region of small strains,

$$\text{stress} = E \times \text{strain}.$$

The quantity E is a constant known as Young's modulus. It is a very important property of the material in question, being a measure of stiffness or resistance to deformation. For many metallic substances the value of E is of the order of 10^{11} dynes/sq. cm. For soft vulcanized rubbers the value of E is of the order of 10^7 dynes/sq. cm. Young's modulus for a substance generally varies with the temperature even for ideally elastic substances.

The concept of a modulus can be generalized to nonideally elastic substances by recognizing that the modulus is a function of time and also to some extent a function of the method of measurement. For example, experiments may be conducted in which the substance is subjected to a fixed extension, and the stress is measured as a function of time. The stress per unit strain necessary to maintain the sample at constant extension will be defined as the stress relaxation modulus $E_r(t)$. Similarly, the substance may be subjected to a constant tensile load, and the extension measured as a function of time, a so-called creep experiment. The stress per unit strain measured by this kind of experiment will be denoted by $E_c(t)$, the creep modulus. Furthermore, vibrational experiments may be carried out in which the substance is subjected to vibrations of period t. From these experiments a complex dynamic modulus $E'(t) + iE''(t)$ may be determined. In actual fact, the vibrations used are generally shear vibrations so that the quantity really determined is $G'(t) + iG''(t)$, where the symbol G denotes shear modulus. For incompressible substances the shear modulus G is equal to one-third of the Young's modulus.

In most cases the moduli $E_r(t)$, $E_c(t)$, and $E'(t)$ are approximately equal. For substances which obey the laws of classical linear viscoelasticity, a determination of any one of these quantities over the entire time scale can be used to calculate the other two time dependent moduli, or indeed can be used in principle to predict the results of any viscoelastic experiment.

During the past several years, my associates and I have accumulated extensive data on the stress relaxation modulus $E_r(t)$ of a wide variety of polymers over a wide temperature range. The following pages present a very brief summary of some of the experimental and theoretical findings arising from this work, previously reported in many scattered papers and Ph.D. theses.

The practical experimental methods for measuring stress at constant extension vary with the magnitude of the modulus (stiffness) and are described in the original papers.

I shall divide the discussion into several parts. Part A will describe the phenomenon of chemical stress relaxation obtained with crosslinked rubbers at elevated temperatures; Part B will be concerned with the stress relaxation properties of linear and crosslinked amorphous polymers over the entire temperature scale; Part C will treat the stress relaxation of crystalline polymers; and Part D will describe some experiments with some special natural polymers and polyelectrolytes.

PART A. CHEMICAL STRESS RELAXATION
(CHEMORHEOLOGY)

All very high molecular weight linear polymers which are crosslinked by rather sparse chemical crosslinking bonds into a continuous three-dimensional network structure will, at sufficiently high temperatures, approach a state of "ideal" rubbery behavior. Such materials obey in principle the following theoretically derived equation of state

$$f = NkT[(\ell/\ell o) - (\ell o/\ell)^2] \tag{1}$$

In the foregoing equation f is the force per unit area (based on original cross-section), ℓo is the unstretched length of the rubber sample, ℓ is the stretched length, k is Boltzmann's constant, T the absolute temperature, and N is the number of network chains per cc. A network chain is the portion of the network between contiguous crosslinks. The quantity N can be determined for a given rubber by measuring the force required to obtain the relative extension $\ell/\ell o$ and applying Equation (1). It can also be determined from the amount of cross-linking agent used per gram of linear polymer. For example, when tetrafunctional crosslinks are introduced between "infinite" linear polymers the concentration of network chains is twice the concentration of crosslinks. The two methods give comparable results.

Equation (1) is derived on the basis of the experimentally proved fact that the stress in a stretched sample of rubber arises from a decrease of entropy during stretching. The entropy decrease is, in turn, related to the configurational possibilities of the randomly coiled molecular chains.

It might be expected that for chemically crosslinked rubbers in the temperature region of rubbery behavior, the stress relaxation curves $E_r(t)$ should remain constant with time, inasmuch as thermoplastic flow is suppressed by the crosslinks. In actual fact we discovered that all rubbers show $E_r(t)$ curves that decay to zero stress at sufficiently high temperatures, and we attributed this stress decay to chemical reactions such as chain scission by oxidative cleavage or reorganization of the network structure by ionic interchanges[1,2]. These scissions or bond interchanges will, in general, occur at any place along the chain or in certain cases they may occur preferentially at the crosslinks. In any given instance chemical decay of stress measures the rate of breaking of the weakest chemical bonds in the network structure.

Scission of network chains or bond interchange between neighboring chains will reduce the number N of effective chains maintaining the stress in Equation (1). I have shown that the relation between the number $q(t)$ of bond cleavages that have occurred up to time t in each cc. of rubber and the relative stress decay is

$$q(t) = - N \ln [f(t)/f(o)] \tag{2}$$

where $f(t)$ is the stress at time t measured in a sample maintained at fixed extension $\ell/\ell o$, $f(o)$ is the initial stress, and N is the initial number of network

chains per cc. of rubber[3].   The quantity $[f(t)/f(o)]$ is independent of the relative extension up to values of $\ell/\ell o$ of at least 2.5[1].

A fundamental distinction can now be made between those cases where the bond cleavage is specifically at the network crosslinks and those much more frequent cases where bond cleavage occurs at random among the bonds along the network chains.   If bond cleavage were to occur at network junctures only, the quantity $q(t)$ would be proportional to the concentration of crosslinks and hence would be proportional to N, the concentration of originally present network chains.   The relative stress decay $[f(t)/f(o)]$ would in this case be independent of N in a series of rubbers that were identical save for different values of N, i.e., different concentrations of crosslinks.   This can readily be seen from Equation (2).

If, on the other hand, bond cleavage were to occur at random among the bonds of the network chains, the quantity $q(t)$ would be essentially independent of the number of crosslinks which are quite sparse, and therefore $q(t)$ would be independent of N.   In this case according to Equation (2), $\ln [f(t)/f(o)]$ would
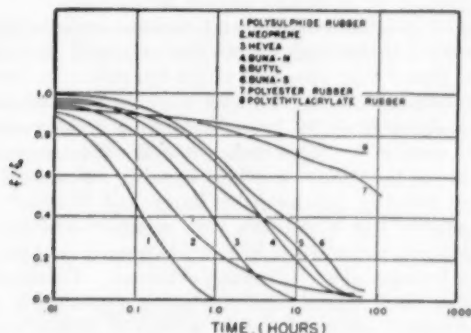
FIG. 1.—Chemical stress relaxation for various vulcanized rubbers at 130° (reference 24).

be inversely proportional to N.   However, an experimental verification of this simple relation is often complicated in practice by the fact that the introduction of crosslinks, as in vulcanization by sulfur-accelerator recipes, often involves the addition to the rubber of reagents that may be positive or negative catalysts for the cleavage reactions along the network chains; i.e., the vulcanizing ingredients are known in many cases to be pro-oxidants for the chain reactions involved in cleavage of hydrocarbons induced by molecular oxygen.

If the rate of bond cleavage is constant, i.e., $q(t) = ct$, then from Equation (2) the decay curves due to chemical stress relaxation obey the decay law:

$$[f(t)/f(o)] = \exp(-k't)k' = c/N = A' \exp(-E^*/RT) \qquad (3)$$

Equation (3) has been found to apply fairly well to many experimental results.   If Equation (3) applies, a plot of $[f(t)/f(o)]$ vs. $\log t$ has a characteristic shape, the major portion of the decay occurring in two cycles of logarithmic time.   Even if Equation (3) is not obeyed exactly, it is characteristic of chemical stress relaxations when plotted in this way to show a major portion of the decay within no more than approximately three cycles of logarithmic time; this is in sharp contrast to stress decay in linear polymers occurring by molecu-

lar flow which generally extends over very many cycles of logarithmic time. Various examples of chemical stress relaxation plotted as $[f(t)/f(o)]$ vs. log t are shown in Figure 1 which will be discussed more fully later on.

CHEMICAL STRESS RELAXATION INDUCED BY MOLECULAR OXYGEN

In many of the hydrocarbon rubbers including natural rubber, GR-S, Buna N, Butyl rubber, and Neoprene, the chemical stress relaxation is brought about by a cleavage induced by molecular oxygen. This is proved by the fact that the rate of stress relaxation can be slowed down by a factor of fifty or more in these rubbers if the experiments are carried out in highly purified nitrogen[1,4]. This is true for sulfur cures as well as for nonsulfur cures[4], contrary to a recent publication by Berry and Watson[5]. It is important to note that the rate of stress relaxation is independent of oxygen pressure over a wide range of pressures, so that there is no difference in stress relaxation studies carried out in commercial nitrogen containing as much as 1 per cent of oxygen and in air[1]. It is also important that the experiments be made with sufficiently thin samples so that the penetration by molecular oxygen is complete.

Many studies of chemical stress relaxation were carried out with these rubbers in order to get a better insight into the nature of the oxidative scission reaction. It was found that chemical stress relaxation in Hevea, GR-S, and Butyl rubber was little affected by whether the vulcanization was accomplished by sulfur and accelerators or by nonsulfur curing recipes such as p-quinone dioxime and lead dioxide[1,6]. This makes it difficult to accept the conclusion that scission occurs at the sulfur crosslinks in sulfur vulcanized natural rubber, a hypothesis very recently put forth by Berry and Watson[5]. In my earlier work, I had considered this hypothesis very seriously and rejected it in favor of a random oxidative scission of the hydrocarbon portion of the network chains in natural rubber because of the foregoing evidence. Furthermore, unvulcanized natural rubber itself shows rapid oxidative degradation at the temperatures at which chemical stress relaxation is usually carried out, showing that scission can and does occur in the pure hydrocarbon.

Oxidative scission as measured by stress relaxation is considerably slowed down by suitable antioxidants[7] and accelerated by pro-oxidants such as peroxides. It was found that many vulcanization accelerators such as tetramethylthiuram disulfide and diphenylguanidine, when rubbed on the surface of the rubber samples, speeded up the chemical stress relaxation and the rate of oxygen absorption[6], presumably by acting as catalysts for the oxidation chain reaction.

While scission is occurring at the elevated temperatures in these hydrocarbon rubbers, there is a crosslinking reaction that is occurring simultaneously. In many cases the crosslinking reaction is a part of the same radical chain reaction induced by molecular oxygen which is also responsible for scission. In some cases the crosslinking reactions may be relatively independent of the scission reaction, e.g., continued vulcanization by unreacted curing agents.

Fortunately, these two reactions, scission and crosslinking, can be examined by physical measurements in the same apparatus. Decay of stress at constant extension measures the scission reaction alone, even though crosslinking is occurring simultaneously. On the other hand, if the sample is kept in a relaxed condition at the elevated temperature and the modulus or the stress required to attain a definite extension is measured intermittently, the net effect of crosslinking and scission is measured. In rubbers in which crosslinking predominates over scission the intermittent modulus increases with time; in rubbers in which

scission predominates the intermittent modulus decreases with time[1,5]. The concept of simultaneous scission and crosslinking originally introduced in these studies to explain the physical changes in polymers produced by high temperatures and oxygen now plays a vital role in the interpretation of changes produced in polymers by high energy radiation.

Thin samples of rubber maintained in a stretched condition at elevated temperatures develop an irrecoverable permanent set because of the simultaneous crosslinking and scission reactions. The permanent set can be predicted from the continuous relaxation curves and the intermittent measurements of the modulus[9].

CHEMICAL STRESS RELAXATION RESULTING FROM BOND INTERCHANGE

The polysulfide rubbers (Thiokols) are crosslinked polymers whose basic structures are:

$$\cdots RS_zRS_zRS_z\cdots,$$
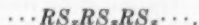
where R is a hydrocarbon residue, S_z refers to monosulfide, disulfide, trisulfide, and higher disulfide linkages that occur statistically distributed along the chains.

In the polysulfide rubbers there is a continuous metathetical interchange of disulfide linkages of the types shown below. Trisulfide and higher polysulfide linkages are also involved in these interchanges.

$$RSSR + R^1SSR^1 \xrightarrow{\text{Cat}} R^1SSR + RSSR^1$$

$$RSSR + R^1SH \xrightarrow{\text{Cat}} RSSR^1 + RSH$$

$$RSSR + R^1SNa \longrightarrow RSSR^1 + RSNa$$

$$RSSR + R^1SPbSR^1 \longrightarrow RSPbSR^1 + RSSR^1.$$
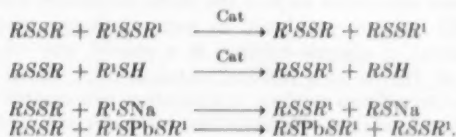
Such interchanges between bonds of adjacent network chains or between an interior bond of a network chain and a terminal group of a network chain do not affect the overall structure of the rubber or the physical properties measured by short time experiments. For example, the intermittent modulus shows no change with time due to these exchanges. It should be stated, however, that a slow change of weight of the substance might occur because low molecular weight ring compounds are formed in the interchange which volatilize over a long period of time unless the sample is kept in a closed oven.

As mentioned in the foregoing, if the rubber were always maintained in an unstressed condition, there would be no very simple means of inferring that these exchanges were occurring. If however, the rubber is stretched to a constant length and maintained at that length, these interchanges will allow the network structure to come to equilibrium with its new strained condition, and so there will occur a relaxation of stress to zero. The situation is analogous, on a different time scale, to what occurs in liquid flow. It is not immediately obvious that the molecules in an unagitated beaker of water are continually exchanging places. This becomes much more apparent if the water is poured into a new shape of container. Just as the water poured from one container to another is identical in its properties before and after, so too is a sample of polysulfide rubber which has been stretched to a fixed length and allowed to decay

to zero stress identical in its properties with the original material except for its shape.

Our studies on stress relaxation of polysulfide rubbers led us to announce the existence of this interchange reaction[2,10]. This reaction was independently and simultaneously postulated by Fettes, Davis, and Bertozzi of the Thiokol Corporation, who observed that when two polysulfide polymer latexes of different structure were mixed, a copolymer was formed under suitable catalytic conditions[11].

We continued our studies of this interchange by studying the reaction between propyl disulfide and propyl mercaptan[12,13]. It was found that the uncatalyzed exchange was a slow reaction, even at 140° C. The rate was not appreciably accelerated by addition of a radical producing catalyst such as benzoyl peroxide. However, the reaction became quite rapid even at room temperature upon the addition of ionic catalysts such as $AlCl_3$ or sodium butyl mercaptide[12].

I attribute the rather rapid chemical stress relaxation of polysulfide polymers to ionic impurities remaining from the polymerization and vulcanization; these impurities serving to catalyze the interchange reactions. Very substantial improvement in the chemical stress relaxation of these materials can be achieved by modifying the cure of these polymers in such a way as to avoid having strong acids, bases, or soluble ionic salts as by-products of the cure[10,14]. In fact, the relaxation rates can be slowed down a hundred fold by using diisocyanates as curing agents[14] as compared with lead peroxide cures.

In 1947 our studies on the stress relaxation at high temperatures of vulcanized silicone rubbers convinced us that the stress relaxation was due to an ionic interchange of SiO linkages catalyzed by some unknown reagent[15]. In 1950 we prepared crosslinked silicone rubbers in a special way which unavoidably contained traces of H_2SO_4 as a residual catalyst[16,17]. These rubbers showed complete decay to zero stress at room temperature in a matter of several minutes unless the residual catalyst was stabilized by water or pyridine. The water was reversibly removable at low relative humidities and was therefore a useful stabilizer only at high relative humidities. On the other hand, pyridine was a permanent stabilizer. Once stabilized these specially prepared silicone rubbers showed practically no stress decay even at quite elevated temperatures.

The interchanges under consideration are of the following type:

$$
\begin{array}{ccc}
\text{CH}_3 & \text{CH}_3 \\
| & | \\
R\text{---O---Si---O---}R + R^1\text{---O---Si---O---}R^1 & \xrightarrow{\text{Cat}} \\
| & | \\
\text{CH}_3 & \text{CH}_3
\end{array}
$$

$$
\begin{array}{cc}
\text{CH}_3 & \text{CH}_3 \\
| & | \\
R\text{---O---Si---O---}R^1 + R^1\text{---O---Si---O---}R. \\
| & | \\
\text{CH}_3 & \text{CH}_3
\end{array}
$$
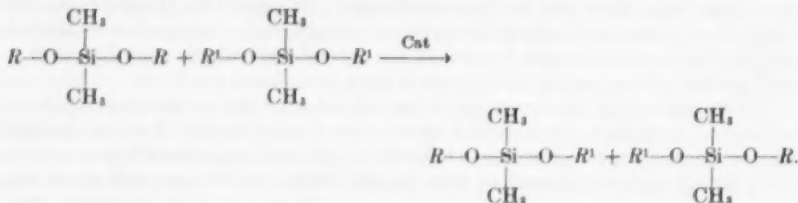
A recent paper has identified the trace catalyst that causes exchange at elevated temperatures in commercially prepared silicone polymers as benzoic acid which comes from the decomposition of benzoyl peroxide which is used as the curing agent[18]. It was shown[18] that radiation cured silicone rubbers showed a much slower rate of stress relaxation.

It is my personal belief that the flow of inorganic silica based glasses at high temperatures is due to an exchange of SiO bonds with other SiO bonds, or pref-

erably an exchange of SiO bonds with O Na bonds, when the latter are present. Thus, I think the concept of chemical stress relaxation transcends the field of organic polymers and is applicable to inorganic substances as well.

In Figure 1 chemical stress relaxation is shown for a number of synthetic crosslinked rubbers at 130° C. The data are plotted in the form $[f(t)/f(o)]$ vs. log t. The rubbers include polysulfide type, Hevea, Neoprene, Buna N, GR-S, Butyl, Lactoprene (polyethylacrylate type) and polyester type (vulcanized with benzoyl peroxide). The tremendous variation in the rate of chemical stress relaxation as between several different synthetic rubbers is clearly seen. Although the stability to reactions at high temperatures is partially inherent in the structure of the polymer, very great variations in stability to chemical stress relaxation have been achieved by suitable purification, incorporation of stabilizers, antioxidants, etc.
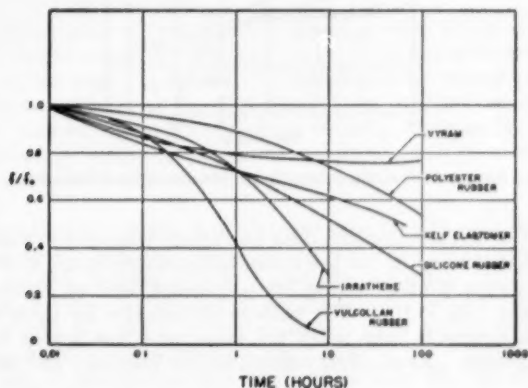
Fig. 2.—Chemical stress relaxation for other vulcanized rubbers at 130°.

Figure 2 shows chemical stress relaxation at 130° C for radiation crosslinked polyethylene (Irrathene), silicone rubber, polyurethane rubber (Vulcollan), Vyram (modified polyacrylate) and Kel F rubber (a copolymer of trifluorochloro-ethylene and vinylidene fluoride). The last two are very resistant to scission of the backbone chains as manifested by their very slow chemical stress relaxation. Crosslinked polyethylene is surprisingly reactive to oxidative scission. Polyurethane rubbers show much faster chemical stress relaxation than polyester rubbers, indicating that the urethane linkages, or more probably the disubstituted and trisubstituted urea linkages found in these polymers cleave more readily than the ester linkages[19].

PART B. STRESS RELAXATION OF AMORPHOUS POLYMERS OVER THE ENTIRE TEMPERATURE RANGE

FOUR REGIONS OF VISCOELASTIC BEHAVIOR FOR AMORPHOUS POLYMERS

The first complete viscoelastic data for any polymer were obtained by stress relaxation studies on polymethylmethacrylate of two different molecular
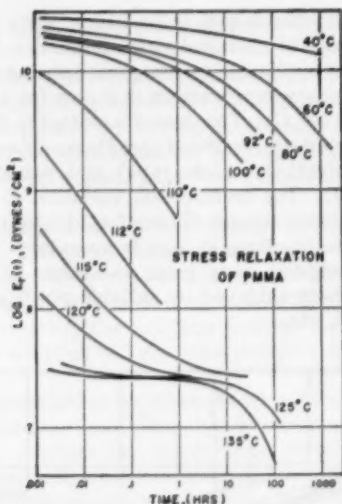
Fig. 3.—Log $E_r(t)$ vs. log(t) for polymethylmethacrylate (reference 20).

weights[20,21]. The stress relaxation data at various temperatures are plotted in the form log $E_r(t)$ vs. log (t) for the entire temperature range in Figure 3. In Figure 4 are shown similar results for polyisobutylene of viscosity average molecular weight 1.35×10^6. The pattern of behavior for these polymers as shown in these figures is very much the same, and this is also true of other amorphous polymers. As was first pointed out by Tobolsky and McLoughlin[20],
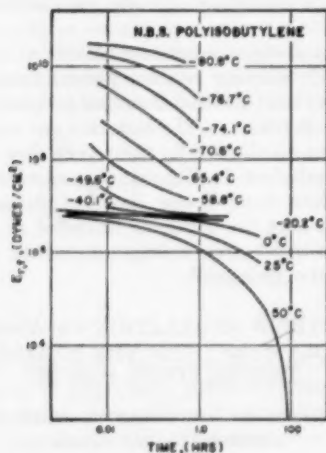
Fig. 4.—Log $E_r(t)$ vs. log (t) for polyisobutylene of molecular weight $\bar{M}_v = 1.35 \times 10^6$ (references 30 and 44).

and can be clearly seen from the figures, there are four clearly defined regions of viscoelastic behavior.

(1) A low-temperature *glassy region* in which the modulus $E_r(t)$ is of the order of magnitude of $10^{10.5}$ dynes/sq. cm. The time effects are not very pronounced in this region so that we may speak of a quasi-static glassy modulus E_1. $E_r(t)$ is fairly independent of molecular weight in this region but depends very markedly on the rate at which the sample is annealed[22].

(2) A *transition region* of elastoviscous behavior in which $E_r(t)$ changes very rapidly with time and temperature, the value of $E_r(t)$ ranging between 10^{10} dynes/sq. cm. and 10^7 dynes/sq. cm. The polymers feel leathery to the hand in this region. The values of $E_r(t)$ are independent of molecular weight in this region for polymers of sufficiently high molecular weights[23]. The time effects in the transition region are due to short range motions of relatively small segments of the polymer molecules.

(3) A quasi-static *rubbery plateau region* in which the modulus $E_r(t)$ is of the order of magnitude of 10^7 dynes/sq. cm. and changes quite slowly with time. The stress in this region appears to be maintained by entanglements between the long chain molecules as was first pointed out in these researches[24]. From the rubbery plateau region a quasi-static rubbery modulus E_2 can be defined and the molecular weight between entanglements can be calculated[25]. The presence of chemical crosslinks will of course increase the value of the rubbery modulus E_2.

(4) A *flow region* in which $E_r(t)$ changes very rapidly with time from values of 10^7 dynes/sq. cm. to zero. The $E_r(t)$ curves in this region are very markedly dependent on the molecular weight and the molecular weight distribution. For samples of the same molecular weight distribution but different average molecular weight $\bar{M}_v$, the $E_r(t)$ curves appear to be shifted horizontally along the log-time axis, the shifting factor being $3.3 \log \bar{M}_v$.[25] For samples of different molecular weight distribution, but the same value of $\bar{M}_v$, the slope of the $E_r(t)$ curve vs. $\log(t)$ curve appears to change, but the relative position along the log-time axis remains the same[24,26].

The time effects in the rubbery flow region are due to motions of the molecules as a whole or to very large molecular segments.

When the chemical cross linking between the linear chains is sufficient to form a continuous three dimensional structure, the flow region is completely suppressed, to be replaced at higher temperatures by a region of chemical flow due to breaking of primary valence bonds by oxygen, by ionic interchanges, or by other means.

TIME–TEMPERATURE SUPERPOSITION PRINCIPLE

The time-temperature superposition principle whereby viscoelastic data at one temperature are transformed to another temperature by a simple multiplicative transformation of the time scale[8,25,27,28] was independently proposed by Tobolsky and Andrews[8] and by Leaderman[27]. In its simplest form this principle means that curves of $E_r(t)$ or $\log E_r(t)$ vs. $\log(t)$ that are obtained at different temperatures are superposable by means of a horizontal shift along the $\log(t)$ axis. Refinements on this procedure are treated elsewhere[29,30].

By means of this principle it is possible to extend the values of $E_r(t)$ obtained at any temperature to both shorter and longer times than can be obtained experimentally. Master curves of $\log E_r(t)$ vs. $\log(t)$ can be constructed that

are applicable for all temperatures and all times. Figure 5 shows a somewhat schematized master curve for unfractionated polyisobutylene of three different average molecular weights. The graph as it stands is valid for 25° C because the log-time origin [log $(t) = 0$] is directly under the indicated marks for 25° C. The master curve for any temperature shown on the graph can easily be obtained by sliding the log-time axis to the new indicated origin. The number of decades of time comprised in this master curve is truly staggering. The validity of the time-temperature superposition principle will be proved later when relaxation modulus and dynamic modulus are compared.

PARAMETERS DEFINED BY THE RELAXATION MASTER CURVES

Stress relaxation data such as are embodied in Figures 3, 4, and 5 can be used to define certain parameters that are characteristic of the polymers being studied[21]. In the first place we have E_1 and E_2, the quasi-static glassy modulus and the quasi-static rubbery modulus. At any temperature T the time re-
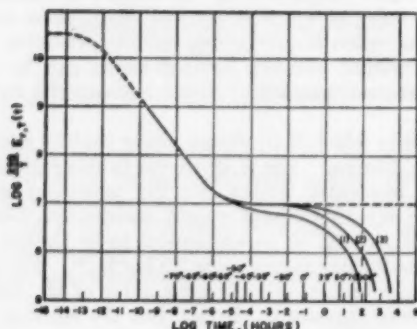
Fig. 5.—Idealized master relaxation curve log $E_r(t)$ vs. log (t) for polyisobutylene of three different average molecular weights (1) $\widehat{M}_v = 1.36 \times 10^6$ (2) $\widehat{M}_v = 2.80 \times 10^6$ (3) $\widehat{M}_v = 6.60 \times 10^6$ (reference 21).

quired for the function $E_r(t)$ to reach the value (log E_1 + log E_2)/2 was called the characteristic relaxation time K[21]. K is obviously a function of temperature $K(T)$. An attempt was also made to define a distinctive temperature T_d from the $E_r(t)$ curves which would correspond in some way to the glass transition temperature T_g obtained from volume-temperature curves. As is well known, evidence exists which indicates that the T_g value obtained from V-T curves depends on the rate at which specimen is cooled or heated. It was hoped that the log $E_r(t)$ vs. log (t) curves would provide a value of T_d that did not depend upon time effects. T_d was defined as the temperature at which $K(T)$ had a maximum value of apparent activation energy. The apparent activation energy is defined as $R[d(\ln K)/d(1/T)]$. A difficulty that arises with this definition is that the time-temperature superposition principle very probably becomes only partially valid at temperatures close to T_d and lower. The horizontal shifts along the log-time scale which produce superposition of the log $E_r(t)$ curves for temperatures below T_g may well be valid only for the time scale of the relaxation experiments. Nevertheless, the values of T_d obtained by the method described above seem to be very close to the T_g values obtained

from V-T curves, at least for the polymers we have studied thus far.   The determination of T_d appears to have experimental, operational validity.

The value of T_g or T_d is a very important characteristic of the polymer, perhaps the most important.   Should our experimental, operational definition of T_d fail for certain polymers, our discussion of these polymers could readily be couched in terms of T_g rather than T_d.

The characteristic relaxation time K at the temperature T_d is denoted by K_d.   An alternative definition for T_d would be obtained if K_d were given the same arbitrary value for all polymers.

An important parameter which characterizes the master relaxation curves is the quantity n, which is the negative slope of the master curve $\log E_r(t)$ vs. $\log (t)$ at the point at which $\log E_r(t) = (\log E_1 + \log E_2)/2$.   Another characteristic parameter is the quantity h, related to n, whose quantitive definition will be discussed subsequently.

TABLE I

PARAMETERS CHARACTERIZING STRESS RELAXATION
OF AMORPHOUS POLYMERS

Polymer	T_d, °K	$\log E_1$	$\log E_2$	n	h	$\log K_d$
Polymethyl methacrylate	384	10.35	7.35	0.52₅	0.31	−1.5
Paracril 26	241.0	10.10	7.40	0.63	0.41₅	−1.54
GR-S	220	10.24	7.44	0.71	0.45	−1.50
60/40 butadiene-styrene	237.1	10.27	8.03	0.50₅	0.40	−1.94
50/50 butadiene-styrene	250.8	10.212	7.558	0.545	0.364	−1.12
30/70 butadiene-styrene	285.1	9.955	7.255	0.55	0.36	−1.13
Polyisobutylene	197.0	10.48	6.88	0.745	0.367	+1.04
(Dynamic)	---	10.52	6.88	0.723	0.352	—
Natural rubber (unvulcanized)	205.3	10.42	7.20	1.07	0.495	−1.90
Natural rubber (vulcanized)	206.3	10.39	7.26	1.10	0.555	−1.095

Table I contains a compilation of the parameters E_1, E_2, h, n, T_d, and K_d for the polymers whose viscoelastic properties have been studied by stress relaxation.

It is, of course, of great interest to inquire how these parameters depend on the molecular structure of the polymers.   Among the polymers studied there does not appear to be a tremendous variation in the values of E_1 and E_2.   The glassy modulus E_1 may well depend upon the strength of the secondary valence forces between atomic groups and upon the amount of free volume in the glass.   Nevertheless, the value of E_1 obtained thus far for various polymers appears to lie in the range 10^{10} to $10^{10.5}$ dynes/sq. cm. E_2 will depend on the chain stiffness in the case of linear polymers and upon the amount of crosslinkage in the case of crosslinked polymers.

The parameter which is of greatest importance in determining the properties of amorphous polymers is T_d or T_g.   To a very crude approximation, one can state that the viscoelastic properties of most amorphous polymers are roughly similar for the same values of T/T_d or $T - T_d$.   The qualitative validity of this principle may be verified by inspecting Figures 3 and 4.   The value of T_d or T_g for any given polymer is determined by the cohesive energy density of the polymer measured by swelling or solubility and the stiffness of the chain which can be measured by light scattering in polymer solutions.   The higher the cohesive energy density the higher is the value of T_d; the stiffer the

chain the higher the value of T_d. The latter point is nicely demonstrated by the fact that polyacenaphthylene has a much higher T_g value than polystyrene.

The quantity n and the related quantity h probably depend upon such factors as the flexibility of the chains and the homogeneity or heterogeneity of composition along the chain. The most flexible polymer chain of all, natural rubber, has the highest value of n determined thus far. It is interesting to note that n seems to increase with increasing chain flexibility whereas T_d appears to decrease with increasing chain flexibility. This may explain the empirically observed relation[22] that for a large group of polymers but not for all the quantity $hT_d \sim 100$. The quantity h is roughly proportional to n.

Although all homopolymers and homogeneous copolymers studied thus far show the qualitative features of viscoelastic behavior described above, polymer alloys or polyblends, which are finely dispersed mechanical mixtures of two polymers just barely on the borderline of compatability, show a splitting of the transition region into two discrete parts[32], as if the polyblend had preserved the two T_d values of each individual component.

It is my belief that not only can one state that the viscoelastic properties of most amorphous polymers are roughly the same for the same values of T/T_d or $T - T_d$, but that this is also true as a crude approximation for strength properties such as elongation at break, tensile strength, impact strength, and so on. This is true in the transition region and the glassy region provided that the molecular weight is sufficiently high. For the rubbery region polymers of comparable crosslink density should be compared for crosslinked polymers, and polymers of the same degree of polymerization, or better, same end to end length, should be compared for linear polymers. It is of course assumed that polymers contain no reinforcing pigments and do not crystallize when stretched. My experience with polymers as diverse as vinyls, polydienes, silicones, fluorocarbons and polysulfides leads me to this qualitative conclusion.

STRESS-BIREFRINGENCE RATIO AND THE MECHANISM OF VISCOELASTIC DEFORMATION

For an ideal crosslinked rubber in the rubbery plateau region of viscoelastic behavior, the stress at constant extension is proportional to the absolute temperature. This means that the entropy of the rubber sample is decreased when the rubber is stretched isothermally, and the stress in the stretched rubber sample actually arises from this decrease in entropy.

The decrease in entropy occurring when a rubber sample is stretched is, in turn, due to a decrease in the long range configurational possibilities of the chain molecules. Since birefringence is also a measure of the long range chain configurations, it is not surprising that the following relation can be derived[34]:

$$\frac{\text{stress}}{\text{temp.} \times \text{birefringence}} = \text{constant}$$

The value of the constant in the foregoing equation can be used to determine the size of the freely rotating segment of the polymer chains[34,35].

It was further shown that the quantity stress/(temperature × birefringence) is a constant independent of temperature and *time* during stress relaxation experiments provided that the experiments were carried out in the rubbery flow region, the rubbery plateau region or the low modulus portion of the transition region[36,37]. This indicates that in these regions of viscoelastic behavior

even during a stress relaxation experiment where stress is changing rapidly with time, the stress must be considered as an entropy stress, arising from long range configurational changes. On the other hand, as one enters the high modulus portion of the transition region and the glassy region, the ratio stress/(temperature × birefringence) changes its magnitude and often changes its sign[36,16]. This indicates that the molecular mechanism of stretching in the glassy region must be different from that operating in the rubbery region. Very probably the stress in the glassy region arises from internal energy changes corresponding to distortion of van der Waals bonds and bending of valence angles, rather than from configurational entropy changes.

This fundamental change in the mechanism giving rise to stress should be taken as an indication that the time-temperature superposition principle may become invalid or only partially valid at temperatures close to and below the glass transition temperature.

MATHEMATICAL FUNCTIONS DESCRIBING $E_r(t)$

The function $E_r(t)$ has been fitted quite well by empirical functions in both the transition region and the rubbery flow region. In the transition region the following empirical function holds very well[31,38]:

$$E_{r \cdot T}(t) = E_r(t/K)$$

$$\log E_r(t/K) = \frac{\log E_1 + \log E_2}{2} - \frac{(\log E_1 - \log E_2)}{2} \, \mathrm{erf}(h \log (t/K)) \quad (4)$$

h = adjustable parameter of the Gauss error function. The quantity h, related to n, has already been considered as one of the characteristic parameters of the master relaxation curve $E_r(t)$.

In the region of rubbery flow the relaxation curve $E_r(t)$ for polyisobutylene at 298° K is fitted quite well by the following empirical function[25,39,40] where $Ei(-x)$ is

$$E_r(t) = E_0[Ei(-t/\tau_3) - Ei(-t/\tau_m)], \quad (5)$$

the exponential integral function, τ_3 and τ_m are parameters that depend on the 3.3 power of the average molecular weight, and E_0 is a parameter that appears to depend upon the molecular weight distribution (see reference 24, p. 448).

For a class of amorphous polymers, notably the butadiene-styrene copolymers, the empirical relation $hT_d = 100$ appears to be valid. When this is true, expressions for $E_r(t)$ which are essentially universal functions of T/T_d can be derived[32]. This reduced equation of state for viscoelastic behavior is not valid for polymers like polyisobutylene where $hT_d \neq 100$.

An extremely simple function which given an approximate fit to the master curve $E_r(t/K)$ in the transition region is

$$E_{r,T}(t) = E_r(t/K) = E_2 + (E_1 E_2)^{\frac{1}{2}} \Big/ \left[\frac{t}{K} + \left(\frac{E_2}{E_1} \right)^{\frac{1}{4n}} \right]^n \quad (6)$$

This function, though not exact, has the advantage of simplicity. Also, all the parameters appearing therein are the characteristic parameters defined in a previous section. Finally, an exact expression for the distribution of re-

laxation times can be obtained[21], and thus the values of any other viscoelastic properties such as E', E'' and η can be calculated by quadrature.

DISTRIBUTION OF RELAXATION TIMES, FLOW VISCOSITY, AND DYNAMIC MODULUS

A distribution function of relaxation times $H(\log \tau)$ can be defined in terms of $E_r(t)$ by means of the following integral equation

$$E_r(t) = \int_{-\infty}^{\infty} e^{-t/\tau} H(\log \tau) d \log \tau. \tag{7}$$

The distribution function $H(\log \tau)$ is very useful since other viscoelastic properties such as the flow viscosity and the real and imaginary components of the dynamic modulus can be calculated therefrom. The quantity ω used below is the angular frequency of vibration.

$$\eta = \int_{-\infty}^{\infty} \tau H(\log \tau) d \log \tau$$

$$E'(\omega) = \int_{-\infty}^{\infty} \left[\frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \right] H(\log \tau) d \log \tau \tag{8}$$

$$E''(\omega) = \int_{-\infty}^{\infty} \left[\frac{\omega \tau}{1 + \omega^2 \tau^2} \right] H(\log \tau) d \log \tau$$

Formulas relating E' and E'' to the distribution of relaxation times were first presented by Tobolsky and Eyring[40,41]. All of these formulas presuppose the validity of the laws of linear viscoelastic behavior. These laws have been proven valid for amorphous polymers but are invalid for crystalline polymers under many conditions.

An idealized distribution of relaxation times at 298° K had previously been presented[40] which had the simple graphical aspects of a box for the rubbery flow region and a wedge for the transition region. The wedge is unaffected by the molecular weight of the sample for sufficiently high molecular weights, whereas the box is shifted along the log-time axis with a shift factor $3.3 \log \bar{M}_v$. Although this idealized function is only an approximation of the true value of $H(\log \tau)$, it has the virtue that exact mathematical expressions for $E_r(t)$ and for E' and E'' can be derived, so that no mathematical approximations are necessary for converting relaxation modulus to dynamic modulus in this case.

A very accurate determination of $H(\log \tau)$ can be obtained from the experimental value of $E_r(t)$ by the use of first- and second-order approximations[30,42-44]. The values of $H(\log \tau)$ at 298° K as a function of $\log \tau$ are tabulated in reference 44.

In Figure 6, I have plotted the exact distribution of relaxation times $H(\log \tau)$ vs. $\log \tau$ for N.B.S. polyisobutylene. Shown on the same figure is the idealized wedge-box distribution. For a fractionated sample, the box becomes narrower and taller as shown schematically by the dotted lines of the figure.

From the distribution function $H(\log \tau)$ obtained entirely from stress relaxation data and the stress relaxation data master curve $E_r(t)$, one can compute and predict the values of $E'(\omega)$ and $E''(\omega)$. Such computations (and
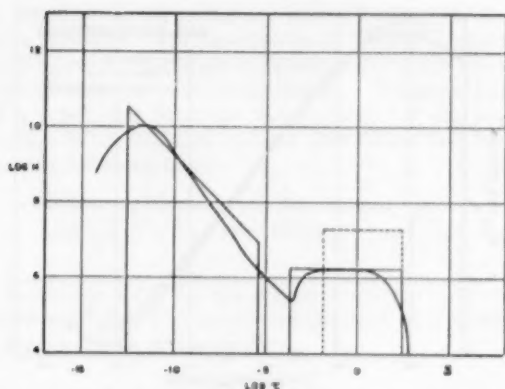
Fig. 6.—Distribution of relaxation times $H(\log \tau)$ vs. $\log \tau$ for N.B.S. polyisobutylene at 25° C. The wedge and box represent the idealized distribution. The dotted box represents the idealized distribution in the rubbery region for a sharp fraction of same $\bar{M}_v$ (references 24 and 40).

tabulations) have been made in references 30 and 44. Figures 7 and 8 show the comparison between predicted values and the experimental values obtained elsewhere[45]. The extremely good agreement provides another verification of the validity of the theory of linear viscoelastic behavior in the case of polyisobutylene. It also provides a verification of the time-temperature superposition principle, because stress relaxation data and dynamic modulus data are obtained in very different time intervals. This is strikingly apparent in Figure 9 which shows stress relaxation data and dynamic data for polyisobutylene obtained at $-44°$ C. The solid curve represents the master curve $E_r(t)$ obtained from stress relaxation data at various temperatures by the time-temperature superposition principle. The agreement between the two types of data is striking.

The relaxation curves of polyisobutylene in the rubbery flow region have been used to predict the bulk viscosity, using the box distribution as the approximation for the relaxation time distribution in that region[29]. Very satis-
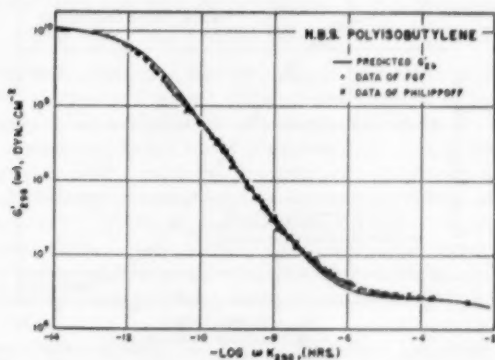
Fig. 7.—Dynamic shear modulus G' vs. negative log frequency for polyisobutylene at 25° C. Comparison of experimental points with solid curve predicted from stress relaxation results (references 30 and 44).
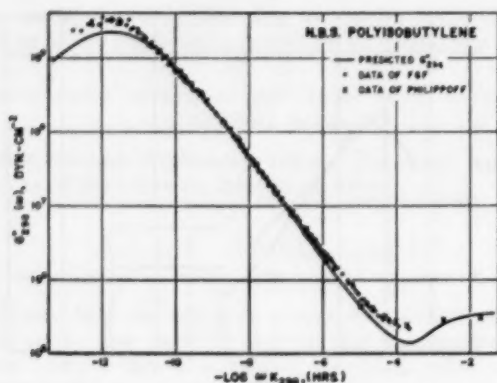
Fig. 8.—Complex dynamic shear modulus G'' vs. negative log frequency for polyisobutylene at 25° C. Comparison of experimental points with solid curve predicted from stress relaxation results (references 30 and 44).

factory agreement was obtained between predicted and experimental values of viscosity.

The distribution of relaxation times corresponding to Equation (6) is [21]:

$$ H(\log \tau/K) = \frac{2.303\,(E_1 E_2)^{\frac{1}{2}}}{\Gamma(n)} \left(\frac{\tau}{K} \right)^{-n} \exp\left[-\frac{(E_2/E_1)^{\frac{1}{2}n}}{(\tau/K)} \right] \tag{9} $$

CHARACTERISTIC RELAXATION TIME $K(T)$ AS A FUNCTION OF TEMPERATURE

It is clearly very desirable to express the temperature variation of $K(T)$ in a manner that would be applicable to all linear polymers. Catsiff and Tobolsky had suggested that $h \log (K(T)/K_d)$ vs. T/T_d should be the same for all amorphous polymers[32,33]. Recently Williams [46] had proposed that $\log a_T$ vs. $T - T_s$
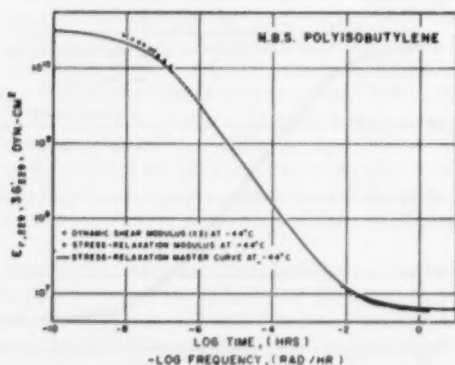
Fig. 9.—Dynamic shear modulus (times three) vs. negative log frequency and stress relaxation modulus vs. log time for polyisobutylene at −44° C. Solid curve represents the stress relaxation master curve. Shear modulus G' is multiplied by three to convert to a tensile modulus.

is a universal function for all polymers, where T_s is a reference temperature selected for each polymer. The function a_T is linearly proportional to $K(T)$. The two theories discussed above are in agreement over the limited temperature interval over which they were commonly tested. Williams, Landel, and Ferry have ascribed a functional form for the variation of $\log a_T$ with $T - T_s$.[43] Expressed in terms of the notation and the parameters used in this article this new theory has the following form:

$$\log \left[K(T)/K_d \right] = - 16.14 \frac{T - T_d}{56 + T - T_d} \tag{10}$$

All of our values for $K(T)$ for the polymers studied by stress relaxation fit this formula very well[30,44]. The agreement obtained with this formula and the experimental data is shown in Figure 10.
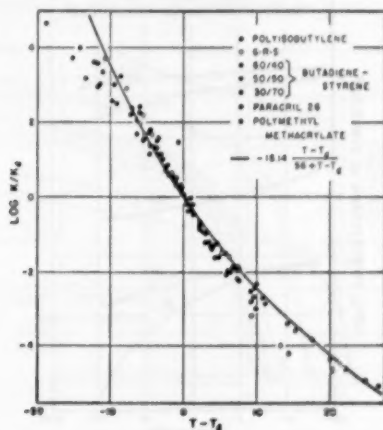
Fig. 10.—Log $K(T)/K_d$ vs. $T - T_d$ for several polymers (references 30 and 44).

PART C. STRESS RELAXATION OF POLYCRYSTALLINE POLYMERS: POLYTRIFLUOROCHLOROETHYLENE

In the previous discussion of the viscoelastic properties of linear amorphous polymers, it was shown that certain features are common to the behavior of all of these polymers. In particular, it was shown that there are four characteristic regions of viscoelastic behavior: a glassy region, a transition region, a rubbery plateau region, and a rubbery flow region. In Figure 4 which presents $\log E_r(t)$ vs. $\log (t)$ for polyisobutylene the behavior in the transition region is to be especially noticed. In the time scale of the relaxation experiments (0.01 to 10 hours) the transition region occurs in the temperature interval between -80 and $-40°$ C, a matter of 40 degrees. In this interval the modulus changes very rapidly with time and temperature between values of 10^{10} dynes/sq. cm. and 10^7 dynes/sq. cm.

Polytrifluorochloroethylene is a polycrystalline polymer whose melting temperature T_m is 215° C. Its glass transition temperature has not been accurately determined but should be somewhere in the neighborhood of room

temperature if the approximate relation $T_g = (2/3)T_m$ is valid. Figure 11 shows stress relaxation data for polytrifluorochloroethylene[48] in the temperature range between 30° C and 193° C. In this interval the modulus varies from $10^{10.1}$ dynes/sq. cm. to $10^{7.2}$. It is particularly interesting to contrast Figures 4 and 11. In Figure 11 the $\log E_r(t)$ vs. $\log (t)$ curves between 30° C and 144° C are relatively flat; i.e., the modulus change with time is much smaller for the polycrystalline polymer as compared to the amorphous polymers. Also in Figure 11 the value of $\log E_r(t)$ at $t = 0.01$ hour changes from a value of $10^{10.1}$ dynes/ sq. cm. at 30° to a value of $10^{8.35}$ at 144°, a very gradual change. The transition region, if such it can be called, for a polycrystalline polymer extends over a much wider temperature range than for an amorphous polymer. The transition region blends into a high modulus rubbery region at high temperatures, crystallites playing the same role in the polycrystalline polymer that
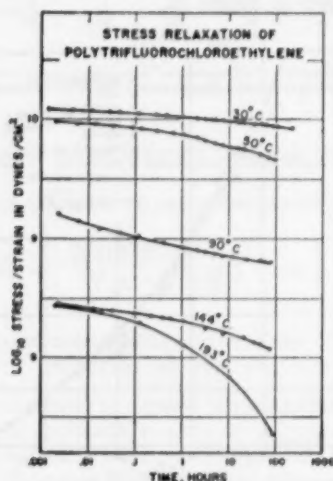
FIG. 11.—Log $E_r(t)$ vs. log (t) for polytrifluorochloroethylene (reference 50).

entanglements or crosslinks do in the amorphous polymers.   The crystalline "crosslinks" are temperature sensitive, but in some cases they may be relatively stable with time at a fixed temperature.

Because there are changes with temperature in the microcrystalline structure and in the stress bearing mechanisms, it is certain that the simple time-temperature superposition that is valid for amorphous polymers in the transition region is not valid for polycrystalline polymers.   There is not only a horizontal displacement along the log-time axis due to changing rate of molecular motions with temperature, but also an even more important vertical shift along the log $E_r(t)$ axis due to the changing structure and other factors.

It is interesting to note that the polycrystallinity of plasticized polyvinyl chloride was first discovered by Tobolsky and Stein from an examination of the $E_r(t)$ curves[49].   These rubbery samples behaved like crosslinked rubbers in that $E_r(t)$ was relatively independent of time.   At progressively higher temperatures the values of $E_r(t)$ became smaller, although the time dependence of $E_r(t)$ always was slight.   It was inferred that crystallites were acting as

temperature sensitive but not time sensitive crosslinks. The presence of crystallites was also proven by x-ray, birefringence, and other techniques[49]. Our stress relaxation data obtained with high pressure, branched polyethylene[50] and with low pressure, linear polyethylene show overall characteristics similar to those of polytrifluorochloroethylene.

DECAY OF STRESS AT CONSTANT EXTENSION RESULTING FROM GROWTH OF ORIENTED CRYSTALLITES

The first observations on the decay of stress at constant extension due to the growth of oriented crystalline material were made in this laboratory in 1946[15,51,52]. It was found that vulcanized Neoprene showed very little relaxation of stress after 100 hours at 35° C and 50 per cent extension. However, a complete decay of stress to zero stress was observed after only 50 hours at 0°C and 50 per cent extension—a rude shock to any simple-minded belief that rate of stress relaxation should follow the Arrhenius law in all cases. Actually, the
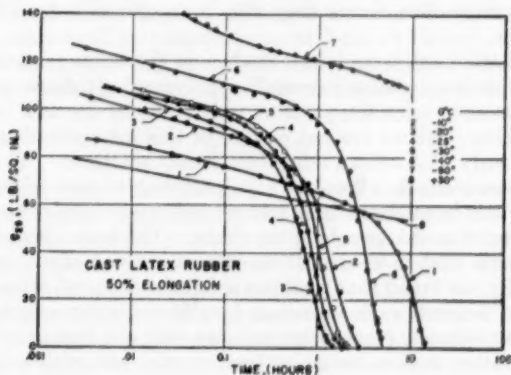
Fig. 12.—Effect of temperature on stress relaxation of unvulcanized natural rubber in the crystallizing region (reference 52).

Neoprene sample after decaying to zero stress began to increase in length beyond the original 50 per cent stretched value, a phenomenon known as spontaneous elongation. This phenomenon was attributed by us to crystallization of the Neoprene. Observations of spontaneous elongation, but no stress decay measurements, were previously reported for natural rubber and for ether polysulfide rubbers[53,54].

An extensive study was made[51,52] on the effect of temperature and elongation on the stress decay curves of unvulcanized natural rubber, cast latex sheet, in the temperature region of crystallization. In Figure 12 stress decay curves are shown for samples maintained at 50 per cent elongation at temperatures of 0, −10, −20, −25, −30, −40, and −50° C. Taking the time required to attain zero stress as an index of the rate of crystallization, it is clear that the results of Figure 12 are in accord with the results of Bekkedahl, who studied the rates of crystallization in unvulcanized natural rubber by a dilatometric procedure[55]. The stress relaxation data show a maximum rate of stress decay at 20° C. At −50° C the rate of crystallization is very slow.

In many crystalline polymers for which no phenomena of spontaneous elong-

ation were observed, the decay of stress was nevertheless accompanied by an increase of birefringence, indicating that even in these cases stress decay may be caused in part by a growth of oriented crystalline material, probably around pre-existing crystal nuclei[49].

I believe that crystallization in silicone rubber at −60° C leads to an *increase* of stress at constant length.

PART D. STRESS RELAXATION STUDIES OF CERTAIN NATURAL POLYMERS AND POLYELECTROLYTES

Our studies of stress relaxation in natural polymers have thus far been rather limited. Natural polymers, as may be expected, show at least all the types of behavior described in the previous sections. Because the natural polymers are generally quite complex, it frequently may happen that it is difficult to decide which molecular mechanism is responsible for the observed stress relaxation behavior. In addition to the previously described mechanisms, transitions from one configuration to another such as $\alpha \rightarrow \beta$ transitions or changes in crystalline forms may also be responsible for observed viscoelastic behavior.

We have carried out some initial studies on the stress relaxation of wool[56]. This natural fiber is an oriented crystalline polymer. It shows a characteristic relaxation in water at room temperature which may be due to a further orientation of crystallites, but we are not certain of this interpretation. It shows a sizeable and nearly Maxwellian relaxation in salt solutions. This may be due to an electrostatic effect. Wool is a polyampholyte and in pure water the chains may be held in some partially folded form due to attraction of alternating positive and negative charges along the chain. The ionic cloud introduced by adding salt would tend to weaken these attractions and cause unfolding of the chains. Finally, we found that wool has a definite chemical stress relaxation in the presence of reagents such as sodium bisulfite or water soluble mercaptans. These reagents obviously react or interchange with the cystine crosslinkages.

Stress relaxation studies have also been carried out with gelatin[57]. Ferry *et al.* have interpreted the results in terms of making and remaking of bonds between collagen chains acting as temporary crosslinks[57]. I feel that gelatin gels are structurally similar to gels of plasticized polyvinyl chloride—namely, they are held together by crystallites acting as crosslinks, and it is this structural aspect that accounts for their rigidity and resistance to flow. Sometimes the relaxation of stress at constant extension for such systems is very slow and the change in birefringence is also very slight, as was found by Stein and Tobolsky for plasticized polyvinyl chloride[36,49]. The crystallites appear to be acting as crosslinks which are quite stable with respect to time, i.e., they do not break and remake at constant temperature. As the temperature is increased the modulus of the sample decreases, indicating fewer crystallites and hence fewer crosslinks. The relative rate of decay of stress, however, is unaffected by the increase in temperature.

Very often, however, the decay of stress in polycrystalline polymers or their gels is accompanied by an increase in birefringence, as was noted in the same study[36,49], indicating that the stress decay was caused by a growth and/or orientation of crystallites. The result with natural rubber at −25° C discussed in Part C is an extreme example of this phenomenon. Interestingly, it has been noted that even when stress decay in a strained gelatin gel was complete some double refraction persisted[55]. For this reason I have been led to postulate that

part of the stress decay in gelatin gels may well be due to the further growth of oriented crystalline material around already existing nuclei[10]. I would expect that if stress decay were due to a breaking and remaking of temporary cross-links, the stress and birefringence would decay at exactly the same rate.

The formation of new crystalline nuclei in strained gelatin should also be considered, as well as growth of oriented crystalline materials around existing nuclei. A theory of permanent set would have to take both these effects into account.

Finally, we have begun some studies of the stress relaxation behavior of collagen in water at various temperatures[26]. At temperatures below 58° collagen is a highly crystalline and highly oriented polymer of high modulus. A relaxed specimen heated in a water bath will show a large and sudden shrinkage at about 58°, which must correspond to a melting or transition temperature T_m, because there is a profound change in the x-ray pattern. The x-ray pattern can be partially but not wholly restored by stretching the shrunken specimens[26]. Since the shrunken specimens are themselves partially crystalline, the transition at 58° may be from one crystal form to another.

We have found that collagen maintained under quite slight tension may be heated in a water bath to temperatures at least 20° above the usual shrink temperature without showing the phenomenon of shrink. We are at present trying to understand this interesting result and, as usual, pursuing the unknown end.

SUMMARY

Extensive studies of the viscoelastic properties of polymers undertaken in the author's laboratory by means of the method of stress relaxation are here reviewed. The discussion is divided into four parts: chemical stress relaxation, stress relaxation in amorphous polymers, stress relaxation in crystalline polymers, and stress relaxation in certain natural polymers and polyelectrolytes. Mathematical description of the phenomena are presented in simple form. The relation between structure and viscoelastic properties of polymers are discussed and a rather complete over-all picture of these phenomena seems to be emerging.

ACKNOWLEDGMENT

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APPARATUS FOR THE DIRECT DETERMINATION OF THE DYNAMIC BULK MODULUS *

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INTRODUCTION

The existence of a complex bulk modulus, or a viscosity associated with a pure volume deformation, has been demonstrated for many liquids and for a few rubberlike solids[1]. Most experimental determinations of this property have involved the measurement of the velocity and attenuation of compressional waves, which involve shearing as well as dilatational deformations. Since the attenuations required for determining the viscous component of a modulus associated with propagation of a wave are difficult to measure precisely, the determination of a bulk viscosity which involves the difference between two such quantities is inevitably subject to a considerable uncertainty.

An apparatus for the direct measurement of the dynamic bulk modulus, both the real and imaginary parts, from 50 to 10,000 cps is described here. A similar apparatus, operating in a lower frequency range, has been described by Philippoff and Brodnyan[2].

Bulk modulus, as used here, refers to the slope of the curve relating pressure to fractional change of volume. As discussed in detail previously[1] one can define a complex or frequency-dependent bulk modulus for a sinusoidal time variation of pressure and dilatation in a manner entirely analogous to the definition of a complex shear modulus, as the ratio of the normal components of the stress and strain tensors. If this ratio is frequency dependent, the bulk modulus ($K^* = K' + jK''$), or its reciprocal the bulk compliance ($B^* = B' - jB''$), will contain an imaginary component[3] corresponding to an energy loss or viscosity associated with volume deformation.

The method developed is based on a direct measure of the ratio of the rate of change of volume with time (volume velocity) to alternating pressure during a deformation of the sample which involves a change of volume only. Experimentally, this was realized by confining within a cavity (small compared to a wavelength of sound at the frequency of measurement) the sample, a generator of volume velocity, a detector of alternating pressure, and a confining fluid. The generator and detector were piezoelectric crystals acting as thickness expanders with a net volume change. The transmitting medium used was a light oil with essentially zero shear modulus and a low shear viscosity, and the size of the cavity was limited to the order of 0.1 wavelength at 10,000 cps (in the transmitting medium). Thus the force transmitted to the sample was essentially a hydrostatic pressure. Under these conditions the crystals may be regarded as generating and detecting pure volume deformations. The complex compliances of the crystals, the cavity, the confining liquid, and the sample are additive; the real and imaginary parts of the ratio between input and output

voltages are equal to the real and imaginary parts of these compliances times an apparatus constant.

To eliminate the effect of very small air bubbles, which could not be avoided by any filling technique tried, a static pressure of 100 kg./sq. cm. or more was applied. This apparently forces any air within the cavity into solution in the transmitting medium, and yields reproducible results which are of the order of magnitude calculated from constants given in the literature[4] for crystals of a type similar to those used.

This static pressure must be known with fair precision, since the compressibility of many materials used in the cavity will vary markedly with pressure. Another point to be noted is that the modulus measured here will be an adiabatic, rather than the isothermal one obtained in determinations of static compressibility.

APPARATUS

The cavity was made by forming a cylindrical hole 0.625 in. in diameter and 0.312 in. deep on one face of each of two blocks of steel 6.0 in. in diameter and 1.75 in. thick. The two blocks were clamped together by means of eight
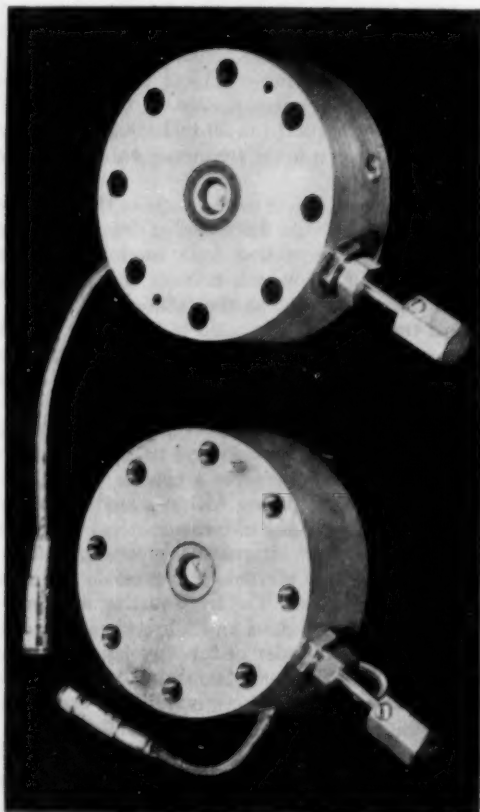
Fig. 1.—Bulk modulus apparatus, disassembled showing cavity and crystals.
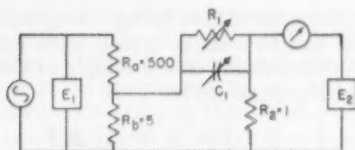
FIG. 2.—Potentiometer circuit.

cap screws, with a soft copper ring in one block and a mating groove in the other forming a pressure seal. To prevent mechanical coupling through the body of the cavity, the crystals were mounted on compliant helical copper springs which in turn were soldered to steel rods passing through seals of a type[5] suggested to us by C. E. Weir. Electrical connections were made through these steel rods and the body of the cavity, to which the surfaces of the crystals facing each other were grounded by fine copper wires.

The crystals were small cylindrical disks with a diameter of 0.5 in. and a thickness of 0.080 in. They were mixed titanates containing 83.4% Ba, 8.6% Ca, and 8.0% Pb. This mixture gives a material with constant dielectric and piezoelectric properties over a wide range of temperature; the Curie temperature is below $-40°$ C[6]. The flat surfaces of the crystals were coated with DuPont Silver 4731 conducting paint, baked at 700° C, and polarized at 50,000 v./in. at room temperature for 60 min.

Provision was made for filling the cavity with Cenco Hyvac oil, the liquid used as a transmitting medium, and for bleeding the air through small holes which could be closed off by needle valves built into the blocks. The whole assembly was found to maintain a static pressure of at least 1000 kg./sq. cm. with no apparent leak. The various components can be seen in Figure 1, which shows the two halves of the block.

The block, with the sample in the cavity, was assembled and supported from springs to isolate it from building vibrations. The static pressure was generated with a hand pump[12] and read from a calibrated gauge[14] of 1000 kg./sq. cm. capacity marked in units of 1 kg./sq. cm.

As shown below, the dynamic bulk compliance is a linear function of the complex ratio of input to open-circuit output voltages. To measure this voltage ratio an ac potentiometer circuit, shown in Figure 2, was devised. The crystals, denoted by their input and output voltages E_1 and E_2, respectively, are mechanically coupled through the cavity. The meter shown in series with E_2 is actually a high impedance, battery-powered, differential preamplifier[15] operated with the input floating followed by a frequency analyzer[16] to serve as a selective filter and detector. With this combination the potentiometer can be balanced by adjusting R_1 and C_1 to correspond to a net input signal of about 0.3 μv.; E_2 is about 0.5 mv. for the customary driving voltage, E_1, of 50 v. In a few cases, to obtain a balance, it was necessary to arrange the condenser in parallel with R_2 rather than with R_1.

TRANSDUCER EQUATIONS

The relationship[7] between voltage E, current I, pressure p, and volume velocity u, can be written as a matrix:

$$\begin{bmatrix} E \\ I \end{bmatrix} = \begin{bmatrix} a\ b \\ c\ d \end{bmatrix} \begin{bmatrix} p \\ u \end{bmatrix} \tag{1}$$

where a, b, c, and d are properties of the crystal. In general, they will vary with frequency, temperature, and to a slight extent, with pressure. For a piezo-electric transducer, the determinant of the matrix of the crystal constants is -1, so the reciprocal of Equation (1) is

$$\begin{bmatrix} p \\ u \end{bmatrix} = \begin{bmatrix} -d & b \\ c & -a \end{bmatrix}\begin{bmatrix} E \\ I \end{bmatrix} \tag{2}$$

A subscript "1" will refer to the driving (input) crystal, "2" to the pickup (output) crystal. Under the conditions of use, as previously mentioned, only pressures and volume velocities are considered and shearing motions or forces are absent. Consequently, the properties of the medium in which the crystals are acting may be expressed by

$$\begin{bmatrix} p_i \\ u_i \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ j\omega C_a{}^* & -1 \end{bmatrix}\begin{bmatrix} p_0 \\ u_0 \end{bmatrix} \tag{3}$$

where p_i, u_i are the input pressure and velocity (those associated with the medium adjacent to the driving crystal), p_0, u_0 the output quantities (those associ-
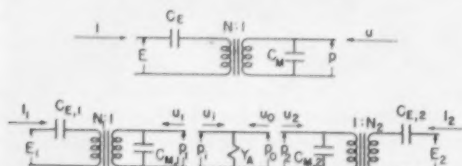
Fig. 3.—Equivalent circuits for a volume expander crystal (top) and for the bulk modulus apparatus (bottom).

ated with the medium adjacent to the pickup crystal), and $C_a{}^*$ is an acoustic compliance equal to the sum of the compliances of the block, the transmitting medium, and the sample.

As the dimensions of the cavity are small enough so that the pressure at any instant is uniform, $p_1 = p_i = p_0 = p_2$. With the convention indicated in Figure 3 that all velocities and currents are to be directed *into* the transducer or medium, $u_1 = -u_i$; $u_0 = -u_2$. Thus, the relation between the currents and voltages of the driving and pickup crystals is found to be

$$\begin{bmatrix} E_1 \\ I_1 \end{bmatrix} = \begin{bmatrix} a_1 & b_1 \\ c_1 & d_1 \end{bmatrix}\begin{bmatrix} 1 & 0 \\ -j\omega C_a{}^* & 1 \end{bmatrix}\begin{bmatrix} -d_2 & b_2 \\ -c_2 & a_2 \end{bmatrix}\begin{bmatrix} E_2 \\ I_2 \end{bmatrix} \tag{4}$$

In particular, if I_2 is held equal to zero, the ratio of input to output voltage is

$$(E_1/E_2)^* = b_1 d_2 [-a_1/b_1 - c_2/d_2 + j\omega C_a{}^*]. \tag{5}$$

If the cavity of volume V contains a sample of volume V_s with compliance $B_s{}^*$ and a volume $V - V_s$ of oil with compliance $B_t{}^*$, Equation (5) reduces to

$$(E_1/E_2)^* = D^*[C^* + (B_s{}^* - B_t{}^*)V_s]. \tag{6}$$

In this equation the term $B_t{}^*V$ has been included in C^* along with terms due to the compliance of the cavity and the terms a_1/b_1 and c_2/d_2 in Equation (5).

From Equation (6) it is seen that a measure of the slopes of the real or imaginary parts of the voltage ratio at any given frequency as a function of V_s, the volume of the sample, will give the differences between the real or imaginary parts of the compliances of the sample and the oil at that frequency, provided the value of D^* is known. To evaluate this constant, it is necessary only to use a sample and transmitting liquid for which the compliances B^* are known.

No assumptions have been made here as to the behavior of the crystal constants (a, b, c, and d) with frequency, temperature, or static pressure.

For crystals operating well below their fundamental resonance, which is the case considered here, an alternate derivation of Equation (6) can be obtained from the equivalent circuits of Figure 3, as pointed out by Mr. B. D. Simmons, formerly with the national Bureau of Standards. Such a derivation leads to the following relations, identical to Equation (6) but expressed in terms of slightly different crystal constants[4] than those encountered in the matrix formulation used above:

$$(E_1/E_2)^* = N_1/N_2 + [1/(C_{E,1}N_1N_2)](C_a^* + C_{M,1} + C_{M,2}) \qquad (6a)$$

The voltage ratio is measured with the circuit shown in Figure 2; the equation for the condition of balance is:

$$(E_1/E_2)^* + 1 + R_a(1/R_2 + 1/R_b) + (1/R_2)(1 + R_a/R_b)$$
$$\times (R_1 - j\omega R_1^2 C_1)/(1 + \omega^2 R_1^2 C_1^2) \qquad (7)$$

The denominator in the last term is essentially unity for all cases encountered. In practice balance is obtained by adjusting R_1 and C_1; terms involving only the other resistors, whose values are shown in Figure 2, are lumped with the final calibration constant of the apparatus. From Equations (6) and (7) we obtain

$$(\partial/\partial V_s)(R_1 - j\omega R_1^2 C_1) = A^*(B_s^* - B_i^*) \qquad (8)$$

where

$$A^* = A' + jA'' = R_2(1 + R_a/R_b)^{-1}D^*$$

Alternately, if Equation (6a) described the behavior of the apparatus, the constant A^* would be replaced by a real, frequency-independent constant. Although it turned out that this simplification was justified over the frequency range used here, it is not introduced at this point, since Equation (6a) also requires that the quantity C^* in Equation (6) should be independent of frequency, which requirement is not met. Therefore, we will use the more general formulation as given by Equation (6) and demonstrate experimentally that the constant A^* is real and frequency independent over a certain frequency range.

CALIBRATION

The adiabatic bulk compliances of the materials used as "standards" for the calibration are listed in Table I. All values are for 25° C and 250 kg./sq. cm., the conditions used in this work. The values for steel and magnesium are essentially independent of temperature and pressure near room temperature and over the limited range of pressure used here. A small correction has been made to the isothermal values measured by Bridgman to convert them to adiabatic, using the standard thermodynamic relation for their difference[5], $TV\alpha^2/C_p$, where α is the (volume) thermal expansion coefficient, V the specific

TABLE I

Material	Bulk compliance (meters²/newton)	Source
Iron (steel)	0.587×10^{-11}	Bridgman[a]
Magnesium	2.90×10^{-11}	Bridgman[a]
Cenco Hyvac oil	46.6×10^{-11}	Litovitz
Rubber-sulfur (RS)	23.8×10^{-11}	Scott[b]

[a] P. W. Bridgman, "The Physics of High Pressure" (The Macmillan Company, New York, 1931), Table V.

[b] See reference 9.

volume, and C_p the specific heat at constant pressure. For the rubber-sulfur sample (natural rubber plus 30% sulfur, vulcanized for 20 hr. at 149° C), the p-V relations of Scott[9] were used to calculate an appropriate isothermal compliance; the necessary quantities for converting this to an adiabatic compliance were taken as $\alpha = 1.93 \times 10^{-4}$ (from a linear coefficient measured by G. M. Martin of this laboratory), $C_p = 0.344$ cal./g./deg. (from observations of McPherson and Bekkedahl[10]).

The value for the oil was obtained from measurements of the velocity of sound under various static pressures carried out by T. A. Litovitz and E. H. Carnevale of the U. S. Naval Ordnance Laboratory using a special interferometer recently described[11]. The measurements yield an adiabatic modulus directly. A correction (of about 1%) to the density measured at one atmosphere was estimated using a relation given in the Smithsonian Physical Tables (p. 284, ninth edition) for a similar oil.

It is to be expected that for all of these materials the bulk compliance will be real and independent of frequency within the frequency, temperature, and pressure ranges considered. The results obtained using steel as a sample and the Cenco oil as the transmitting medium are illustrated in Figure 4, where the absolute value (very nearly the same as the real part) of the voltage ratio is shown as a function of frequency for samples of steel of the volumes shown. The points for the two highest frequencies on each curve were measured at
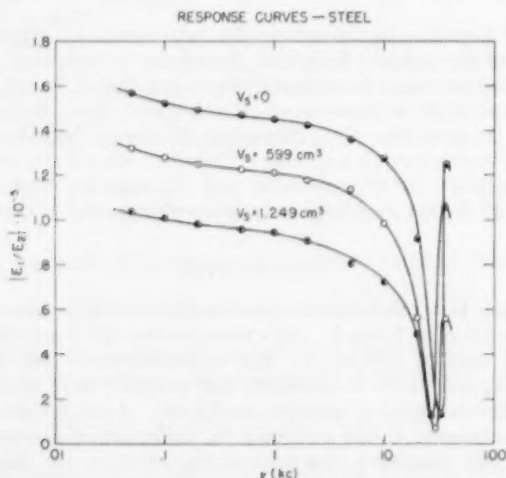
Fig. 4.—Response curves, voltage ratio vs. frequency, steel-oil for several volumes of steel.

minima or maxima of the curves. According to Equation (6a), we should have a line parallel to the frequency axis for any one sample. The shapes of the actual curves indicate that there is a resonance at about 30 kc., which corresponds to a frequency at which the dimensions of the cavity would represent about a quarter wavelength of sound in the oil. When this condition is reached, of course, the assumption that the pressure throughout the cavity is uniform and hydrostatic is no longer valid. Equation (6) with frequency-dependent apparatus constants could hold over a much larger frequency range than Equation (6a), for it would be valid so long as the pressure experienced by the sample (which is, of course, considerably smaller than the cavity) is uniform at any instant. That this is the case is shown by the fact that the vertical distance between the curves for samples of different volumes is constant up to a frequency well above that at which the influence of the resonance become appar-
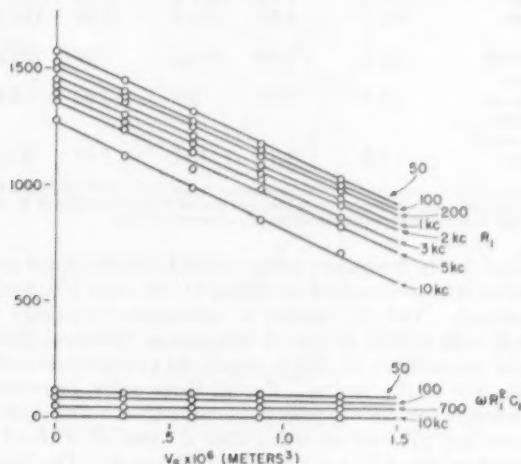
Fig. 5.—Real and imaginary parts of voltage ratio vs. volume of sample, steel-oil.

ent. No serious effort has been made to obtain data above 10 kc., because accurate measurements are made difficult by complicated resonance effects at higher frequencies.

Figure 5 shows data obtained with the potentiometer circuit of Figure 2 for steel-oil systems plotted against volume of sample. R_1 and $\omega R_1^2 C_1$ are shown; according to Equation (8) the slopes of these two groups of lines should equal, respectively,

$$A'(B_s' - B_t') + A''(B_s'' - B_t'') = m'$$

and

$$A'(B_s'' - B_t'') - A''(B_s' - B_t') = m''.$$

It can be seen that the values of m' are nearly identical from 100 to 3000 cps while those of m'' are essentially zero.

Values of $-m'$ and $-m''$, as calculated by least squares, for steel-oil, magnesium-oil, and rubber-oil are shown in Table II. The number of samples shown includes zero volume of the solid in each case.

TABLE II

SLOPES OF VOLTAGE RATIOS VS. VOLUME OF SAMPLE

(All values in mks units $\times 10^{-6}$)

Freq. (cps)	Steel-oil (5 samples)		Magnesium-oil (5 samples)		Rubber-oil (3 samples)	
	$-m'$	$-m''$	$-m'$	$-m''$	$-m'$	$-m''$
50	423.5	14.18	387.7	9.34	223.8	1.34
100	416.2	9.06	387.0	6.78	221.1	6.91
200	411.8	5.90	382.8	7.11	222.0	1.95
500	411.2	6.46	379.8	4.33	221.0	0.78
700	409.9	2.88	379.9	3.05	220.2	$-$ 6.40
1,000	409.6	4.59	380.2	2.48	221.1	$-$ 3.25
2,000	418.8	10.36	377.6	0.90	223.8	-12.87
3,000	417.8	36.5	379.9	0.30	216.6	$-$ 1.91
5,000	438.4	-46.9	361.8	$-$ 5.55	206.0	-12.29
7,000	428.4	1.14	351.6	-17.74	189.7	-14.27
10,000	442.7	4.53	333.2	-12.16	159.3	-17.04
Average (100–3000)	412.9[a]	6.54[a]	381.0	3.56	220.9	$-$ 1.29
Estimated std. dev. s.	3.7[a]	2.78[a]	3.0	2.67	2.2	6.07
Stand. error of the mean $= s/\sqrt{n}$	1.5[a]	1.14[a]	1.13	1.01	0.83	2.30

[a] The values for steel-oil are averaged over the frequency range 100 to 2000 cps, since the 3000 cps values for two of the samples used were obviously out of line, and the oscilloscope pattern of E_1 vs E_2 confirmed the presumption that this measurement was vitiated by an extraneous factor.

The m' values, in the frequency range of 100 to 3000 cps, are nearly constant for all three pairs, with a standard deviation of less than 1%, and appear to be randomly scattered. The m'' values in this same frequency range, which should be zero if both A'' and B'' for all "standards" are zero, yield averages for the steel-oil and magnesium-oil which cannot be taken as zero with the calculated standard error of the means. For all three pairs, however, none of the products involving A'' or $\Delta B''$ appear to be more than 1.6% of $A'\Delta B'$. Within this precision we may proceed assuming that A'' and all of the B''s are zero.

The values of m' vs. $\Delta B'$ are plotted in Figure 6. The line through the origin, whose slope gives us A', was drawn considering only the points repre-
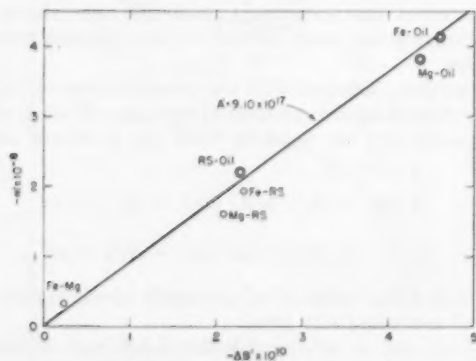
FIG. 6.—Slopes of voltage ratio vs. volume of sample as a function of differences in compliance of several pairs of "standards."

senting direct measurements, which are designated by double circles. The values of m' for the points represented by single circles were obtained by taking appropriate differences between pairs of measured slopes. The only reason for including these points is to demonstrate that the values of B' used for all the four "standard" materials are consistent with each other and with the measurements here. The value of A' from this slope is 9.10×10^{17} mks units, and this is taken as the calibration constant of the apparatus over the frequency range 100 to 3000 cps. Outside of this range the same figure could be used up to 10,000 cps, but a better procedure would be to evaluate a frequency dependent A' (which would be proportional to the m' values) at each frequency.
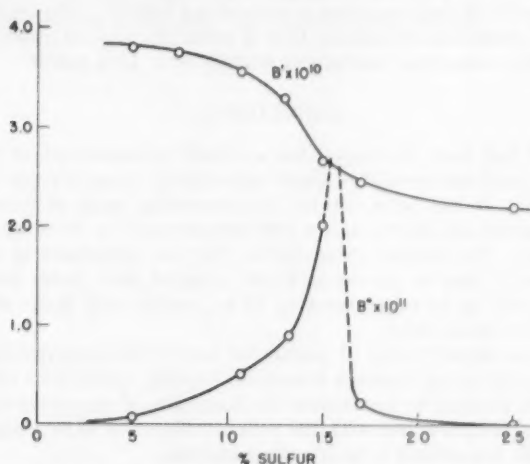
FIG. 7.—Dynamic bulk compliance (sq.m./newton) of natural rubber-sulfur as a function of composition. (To convert to sq.cm./dyne, multiply by .1.)

A plot, similar to Figure 6, showing values of m'' vs. $\Delta B'$ assuming all B'' values as zero, led to a value of A'' of 9.0×10^{15}. This value, of course, is subject to an extremely large percentage uncertainty, and its calculation merely reiterates our previous conclusion that A'' is zero to within about one per cent of A'.

RESULTS ON NATURAL RUBBER–SULFUR VULCANIZATES

To test the method developed it would be desirable to have a single sample which would go through a transition region from rubbery to glassy behavior within our range of variables. So far the measurements have been carried out with frequency as the only variable, since changing either temperature or static pressure would require a complete recalibration.

There is, however, the possibility of going through a transition by changing the composition of the material, and this procedure was chosen to illustrate the capabilities of the apparatus. The system natural rubber–sulfur was chosen, and a series of vulcanizates were prepared by mixing rubber (pale crepe) and sulfur in varying amounts and vulcanizing for 20 hr. at 149° C. This procedure

is known to give essentially complete combination of the sulfur[12].   Such vulcanizates show a glass transition at about 18% sulfur at 25° C, one atmosphere, and for time-scales of the order of minutes or hours.   The conditions of measurement here, with higher pressures and shorter time-scales should lead to a transition at room temperature for a compound with a somewhat lower sulfur content.

The values of B' and B'' for a series of vulcanizates at 25° C, 210 kg./sq. cm., and 700 cps are shown in Figure 7.   At the time of conducting these experiments a resonance at 11 kc. (since eliminated) limited the frequency range of reliable measurements to about 1 kc., but even so the results for the 15% sulfur compound showed B' starting to fall off with increasing frequency, and a sharp rise in B'', the B''/B' ratio reaching a value of 0.1 at 1 kc.   Hence, the B'' curve in Figure 7 is dotted in to indicate that it probably rises to something greater than $0.1B'$ for a compound containing slightly over 15% sulfur.

CONCLUSION

A method has been developed for a direct measurement of the complex dynamic bulk modulus of solid or liquid materials in terms of some known reference standard.   It has been checked by measuring pairs of materials whose static compliances are known and which are assumed to have no appreciable bulk viscosity.   The method gives results (for the differences in compressibility) which are at least as precise as those obtained from static measurements. It can be applied up to a frequency of 10 kc., and a wide range of superposed static pressures can be used.

The method should prove of particular interest in investigating the properties of materials going through transition regions, where time effects are important.   It is planned to investigate the feasibility of operating the apparatus over a range of temperatures with the primary objective of investigating effects associated with transitions in polymeric materials.

SUMMARY

An apparatus has been developed for the direct measurement of the real and imaginary parts of the dynamic bulk modulus of solid and liquid materials over the frequency range of 50 to 10,000 cps. Piezoelectric crystals serving as driver and detector, together with the sample and a confining liquid, are contained in a cavity small compared with the wavelength of sound at these frequencies. Static pressure is superposed to eliminate the effect of small air bubbles.   The complex compliances of the sample, confining liquid, and the cavity, are additive in this region, where the compliance is pure dilatation.   The dynamic compliances of several natural rubber-sulfur mixtures were obtained in a preliminary evaluation of the behavior of the apparatus.

ACKNOWLEDGMENT

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THEORY OF THE NON-NEWTONIAN RHEOLOGY OF RAW RUBBERS CONSISTING OF SUPERMOLECULAR RHEOLOGICAL UNITS *

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INTRODUCTION

Published theories of the viscosity of raw rubbers, or elastomers, deal with the mechanics of the relative movements of the rubber chain molecules[1-3]. However, some recently published work by Mooney and Wolstenholme[4] led to the conclusion that the coherent masses whose relative movements constitute the flow of raw rubbers at moderate rates of shear are of the order 2 to 30 μ in diameter. Such units are 10^6 times larger in volume than the largest of the flow units computed from the Eyring theory of viscosity[5].

If the large volume of the rheological units reported by Mooney and Wolstenholme is accepted as valid, a radical revision of the theory of the viscosity of rubbers seems to be required. The picture of molecular movements occurring at random, but uniformly distributed in the sample, must be replaced by a picture in which the relative movements are concentrated along the interfaces between the rheological units. The required theory may be described, in part, as a theory of the friction between two tacky, elastic solids. Such a theory is presented below.

FRICTION OF TACKY, ELASTIC SOLIDS

The present theory retains the basic element of the Eyring theory of viscosity. Thus, it is assumed that across the interface of two tacky bodies in contact there are attachments, or secondary bonds, which can be broken when there is enough locally concentrated thermal energy to effect a release. However, there is an important difference in the present theory as to the nature and magnitude of the movement following release. Instead of assuming that the movement is of atomic dimensions and the same in each case, it will be assumed that the local surface slippage following bond release is proportional to the bond stress and local elastic strain preceding release, and is usually very large in terms of atomic dimensions.

The precise nature of the bond across a tacky interface does not play a prominent part in the present theory; but the possible nature of the bond should be suggested if the theory is to be accepted as realistic. There are at least four conceivable types of interfacial bonds, one primary and three secondary. A long chain molecule extending appreciable distances on both sides of the interface would be anchored by entanglement with other molecules and constitute a primary interfacial bond. Such a bond would not be broken by chain rupture, as a rule, and would be released only through slow disentanglement of the chains

by a diffusion process.   However, such bonds could form only by a diffusion process; and there would not be time for much chain diffusion between bodies in appreciable relative motion.   Bonds of this type are not considered in the present theory.

One type of secondary bond would be simple mechanical locking due to irregular shape of the chain molecules and the tight packing imposed by the general van der Waals forces and the resulting internal pressure.   Another type of bond would consist of the somewhat tighter packing possible where two or more chain segments are so oriented that they can fit together as in a crystal. Associated with this closer average approach there would be an increased intermolecular force.   A third type of secondary bond would be the hydrogen bond, if the chemical structure of the elastomer is such as to make it possible.

We consider now two elastomer bodies in sliding contact.   In a steady state of relative motion the number of interfacial attachments per unit area will be constant; and also the number of bonds broken and the number formed per unit time will be equal and constant.   In picturing the mechanism of bond release and the effect of bond stress on the process, it will be assumed that relative displacement of two chain segments normal to the interface may produce permanent release; but it is possible also that the two segments may be trapped and return to their original bonded configuration as soon as the local excess thermal energy diffuses away.   The probability of permanent release is increased if the tangential mechanical stress, combined with the thermal energy, produces a displacement with a tangential component.

Following the Eyring[6] method of analysis, we may picture the tangential displacement as being either positive or negative with respect to the direction of the tangential stress.   Then the rate of bond release will be expressed by the equation

$$\frac{dn}{dt} = -\frac{nkTR}{h}\left[\exp\left(-\frac{E-\lambda f}{kT}\right) + \exp\left(-\frac{E+\lambda f}{kT}\right),\right.$$

$$= -\frac{2nkTR}{h}\,e^{-E/kT}\cosh\frac{\lambda f}{kT} \quad (1)$$

where n is the number of bonds left unbroken at the time t after formation, k is Boltzmann's constant, T the absolute temperature, h is Planck's constant, E the activation energy, λ the tangential displacement required for release, f is the bond stress, tangential in direction, and R is the probability of release when the activation energy is supplied. R is the product of the transmission coefficient and the entropy term, neither of which is quantitatively analyzed in the present theory.

It may be noted that two terms in the brackets in the first equation above are added, not subtracted, as in the Eyring theory.   The reason for this difference is that we are concerned here with the total rate of bond rupture, not the excess of ruptures in one direction over those in the opposite direction; for, as has been indicated, we are assuming that the ultimate displacements after rupture are independent of the initial direction of rupture.

The bond stress, f, is not constant, but is assumed to increase linearly with the time since its formation.   Thus,

$$f = pt \quad (2)$$

The proportionality factor, p, will be given a theoretical expression shortly.

With f expressed as in Equation (2), Equation (1) can be integrated, the result being

$$n = n_0 \exp\left(-\frac{\sinh y}{\alpha}\right) \tag{3}$$

where

$$\alpha = \frac{h\lambda p}{2k^2 T^2 R}\, e^{E/kT} \tag{4}$$

$$y = \lambda p t / kT \tag{5}$$

n_0 is the initial number of newly formed bonds at time $t = 0$. For the mean duration of attachment, t_a, we find

$$t_a = \frac{1}{n_0}\int_0^\infty \left(-\frac{dn}{dt}\right) t\,dt = \int_0^\infty \frac{n}{n_0}\,dt = \frac{kT}{\lambda p}\,I_1 \tag{6}$$

$$I_1 = \int_0^\infty \exp\left(-\frac{\sinh y}{\alpha}\right) dy \tag{7}$$

The mean shear stress, τ, on the interface will be

$$\tau = A\int_{-\infty}^t f(t-x)\,\frac{n(t-x)}{n_0}\,dx \tag{8}$$

where A is the number of new interfacial bonds per sq. cm./sec.

Then

$$A = N/t_a \tag{9}$$

N being the existing number of interfacial attachments per unit area at any time. N is assumed to be constant in a steady state of shear.

Obvious substitutions in Equation (8) lead to the result

$$\tau = NkT\rho/\lambda \tag{10}$$

where

$$\rho = I_2/I_1 \tag{11}$$

$$I_2 = \int_0^\infty y \exp\left(-\frac{\sinh y}{\alpha}\right) dy \tag{12}$$

RATE OF INCREASE OF BOND STRESS

An evaluation of p, which is the time rate of bond stress increase, is now required. We consider a mass of rubber subjected to simple shear parallel to the x axis, in the x, y plane. Figure 1 represents a group of rheological units of diameter D, in the shearing material. The relative movements and rotations are indicated by the various vectors. The reference axes are supposed fixed in the center of unit number 1. The solid circle on the y axis represents an interfacial bond between units 1 and 2, the bond consisting of a group of two or more chain segments, at least one of which is from each of the two respective rheological units.

The z velocity of the center of unit 2 will be gD, g being the rate of shear. In addition to being in relative translational movement, all rheological units are also in a state of continuous clock-wise rotation. The rate of rotation is[7]

$$\omega = g/2 \tag{13}$$

Taking the displacement velocities and the angular velocities into account, we find for the difference between the surface velocities of units 2 and 1 at their interface,

$$v_2 - v_1 = gD/2 \tag{14}$$

Since these two relatively moving surfaces are locally bonded at the indicated point on the y axis, the over-all movement must be accompanied by increasing local strains in the neighborhood of the bond. If the strains are
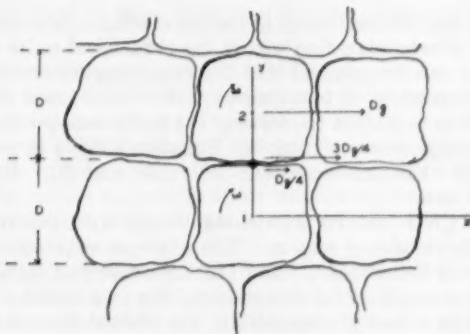
Fig. 1.—Simple shear at rate g of a system of rheological units of diameter D. Reference axes x, y are fixed with respect to the center of unit 1. The surface velocities of units 1 and 2 at their interface are indicated by the vectors $Dg/4$ and $3Dg/4$. The velocity of the center of unit 2 is Dg. All units rotate with angular velocity $\omega = g/2$. The solid circle on the y axis at the 1,2 interface represents an interfacial bond.

equally distributed between the two rheological units, the bonded cluster must have a velocity, v_b, relative to each unit which is half the velocity difference $v_2 - v_1$; or

$$v_b = gD/4 \tag{15}$$

It remains now to find the relationship between the cluster displacement and the stress on the bond which is holding the cluster together. This stress is equal to the elastic stress within a rheological unit acting on that half of the cluster lying within it. The stress can be expressed very simply in terms of identifiable constants when it is recognized that the present problem is analogous to the problem of the velocity of fall of a sphere through a viscous liquid which was solved by Stokes. If an elastic material has a very small shear modulus compared with its bulk modulus, as is the case with rubbers, the equations of elastic equilibriums for small displacements become to a first approximation exactly analogous to the equations of steady state viscous flow for small velocities. Hence, corresponding to Stoke's law, the force required to displace, by the distance δ, a rigid sphere imbedded in a rubber elastic medium is $6\pi aG\delta$, a being the radius of the sphere and G the modulus of rigidity of the rubber.

In the present problem the displaced body is a hemisphere, not a sphere; and hence the force is reduced by a factor $\frac{1}{2}$. The displacement δ will be $v_s t$. From all this it follows easily that the bond stress, f, will be

$$f = 3\pi a g D G t / 4 \tag{16}$$

Hence, p of Equation (2) must be

$$p = 3\pi a g D G / 4 \tag{17}$$

Equation (4) can now be written

$$\alpha = \frac{3\pi a h \lambda D G}{8k^2 T^2 R} e^{E/kT} g \tag{18}$$

According to the kinetic theory of rubber elasticity, the modulus G is proportional to T. Stress relaxation within the rheological units can presumably be ignored. If it can be assumed that the remaining parameters in the above equations are independent of temperature, rate of shear and shear stress, then we are in a position to predict the form of the isothermal g-τ flow curve and its variation with temperature. Thus, by Equation (18), g is proportional to α, and α is related to τ through Equations (10), (12), and (7). By Equation (10) τ is proportional to ρ.

The simplest procedure for comparing theory with experiment is first to prepare a logarithmic plot of ρ vs. α. This of course requires evaluation of the definite integrals of Equations (7) and (12) for a series of values of α. Then a logarithmic plot is prepared for experimental data for τ and g. Since ρ and α are proportional to τ and g, respectively, the plotted data should fit the ρ, α curve after proper vertical and horizontal displacement.

If this is found to be possible, any chosen pair of τ, g values determine a corresponding pair of ρ, α values. The numerical values of certain parameter combinations are thereby determined. Thus, N can be computed from Equation (10) if a value is assumed for λ. The value of t_a can be computed from Equation (6) if values are assumed for λ and for the parameters a, D and G occurring in Equation (17).

E can be computed from Equation (18), if isothermal flow curves have been determined at two or more temperatures. A single point on each of two isothermals is sufficient for the computation. If G is proportional to T, the computing equation is

$$E = k \frac{\Delta \ln (g/\alpha T)}{\Delta (1/T)} \tag{19}$$

Points chosen arbitrarily on different isothermals can be used; but it is clear that the computation is simpler if the choice is such that $\alpha_1 = \alpha_2$. E having been determined, and values of other parameters in Equation (15) having been assumed, R also can be computed.

COMPARISON WITH EXPERIMENT

The flow curves of slightly milled pale crepe Hevea rubber, reported by Mooney[5] and first analyzed by Smallwood[1], are shown again in Figure 2[9]. Some
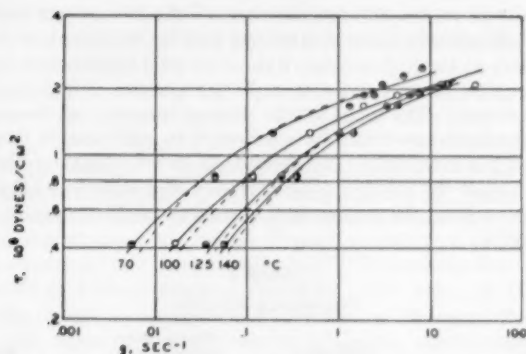
FIG. 2.—Isothermal flow curves for slightly milled Hevea pale crepe.   The full curves are the theoretical curves according to the present theory.   The dashed curves are the best fits by the Smallwood theory.

of the intermediate temperatures are omitted for the sake of clarity.   The full lines show the fit obtainable with the equations of the present theory.   Each isothermal set of points was fitted independently, without regard to the assumed constancy of E.   Calculated values of E, tabulated later, are actually found to be constant within experimental error.   The dashed lines in Figure 2 show the best fit obtainable in like manner with the Smallwood equation.   There is not much difference between the two sets of theoretical curves; but the dashed curves consistently fall away slightly from the experimental points at the lowest stress.   In this respect the full curves are therefore slightly better.

Figure 3 shows some recent flow data obtained with a sample of GR-I-18. The flow data were obtained with a multi-speed disk viscometer (the Mooney viscometer[10]).   Absolute rates of shear and shearing stresses were computed by formulas based on the power law of fluidity, applied after the manner of Piper and Scott[11].

The interesting feature of the experimental curves of Figure 3 is that they are somewhat different in form from those of Figure 2; and the departures from
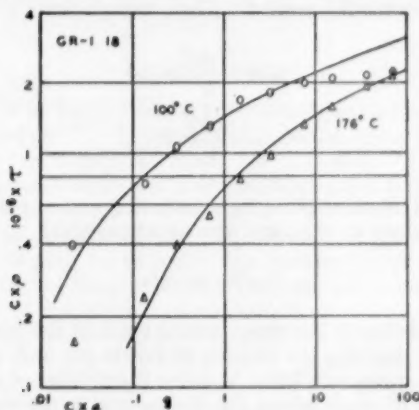
FIG. 3.—Isothermal flow curves for GR-I-18, a Butyl rubber. The curves are theoretical.

the theoretical curves are at opposite ends of the two curves and in opposite directions. Qualitatively these departures can be explained as follows. The fact that the data at the higher rates of shear at 100° C fall below the theoretical curve can be attributed to a decrease in N, the number of interfacial secondary bonds, as g increases. The fact that the data at low rates of shear at 176° C lie above the theoretical curve can be attributed to appreciable development of diffusion across the interface. No theoretical development of these ideas has yet been attempted, to predict quantitatively the observed effects; but it is possible to deduce from the theory as it stands the reduction in N indicated by the data at 100° C.

TABLE I
PARAMETER VALUES[a]

Test material	Pale crepe milled 5 min. (Mooney)	Smoked sheet milled 30 min. (Saunders and Treloar)	Butyl rubber GR-I-18
Mooney viscosity	80[b]	45[b]	80
λ, cm.	1×10^{-8}	1×10^{-8}	1×10^{-8}
a, cm.	5×10^{-8}	5×10^{-8}	5×10^{-8}
$10^4 \times D$, cm.	19	10	20
$10^{-8} \times G$ (at 100° C) dynes/sq. cm.	3	3	1
Computed parameters[c]			
E, kcal/mole	10.1	7.5	10.5
$10^{-11} \times N$, cm.$^{-2}$	1.2	1.0 to 1.4[d]	1.4
$10^3 \times t_a$, sec.	1.2	0.7	2.1
$10^7 \times R$	5	8	9

[a] λ is the range of tangential molecular force opposing bond rupture, a is the radius of the cluster of chain segments in a bond, D is the diameter of the rheological units, G is the dynamic modulus of rigidity of the rheological units, E is the activation energy, N is the number of interfacial secondary bonds per unit area of shear, R is a constant which is the product of the transmission coefficient and the entropy factor.
[b] Estimated from the flow curve at 100° C.
[c] N and R at 100° C, t_a at 100° C, $g = 0.2$ sec.$^{-1}$.
[d] These values of N show a regular trend, varying inversely with temperature, from 50° to 140° C.

To demonstrate this point, we choose a high value of g, for which the theoretical curve and the observed points at 100° C are in disagreement; and we let the subscript 0 designate the observed point and the subscript t designate the theoretical point for the same g. Then, from Equation (10),

$$\tau_0 = \frac{N_0 kT}{\lambda}\, \rho(\alpha_0)$$

$$\tau_t = \frac{N_t kT}{\lambda}\, \rho(\alpha_t) \tag{20}$$

But Equation (15) shows that for constant T and g, α is constant. Hence in the above equations $\alpha_0 = \alpha_t$, and the equations yield

$$N_0/N_t = \tau_0/\tau_t \tag{21}$$

In the present instance the experimental point at the highest rate of shear, 70 sec^{-1}, indicates that N_0, the number of bonds per unit area at this rate of shear, has dropped down to $0.75 N_t$, N_t being the number of bonds per unit area at the lower rates of shear where the theory and experimental points are in agreement.

Theoretical flow curves have been found to fit quite well also the published data of Saunders and Treloar[12] on a sample of smoked sheet Hevea rubber previously milled for 30 minutes.

These data and the data of Figures 2 and 3 have been analyzed by means of the equations of the present theory. The results are shown in Table I. The values of a, λ, D, and G had to be either assumed or estimated from measurements of low precision or of uncertain applicability. For all three rubbers a and λ were assumed to be $a = 5 \times 10^{-8}$ cm. and $\lambda = 10^{-8}$ cm. The values of D for Hevea were obtained from the published data of Mooney and Wolstenholme,[4] after the Mooney viscosities of the two samples concerned were estimated by comparing their flow curves at $100°$ C with the flow curves of other Hevea samples of known Mooney viscosity. The value of D for Butyl was assumed to be the same, approximately, as that of Hevea of the same Mooney viscosity. The value of G for Hevea is Mooney's value computed from the frequency of free oscillation in the rubber rheometer[8]. The value of G for the Butyl rubber is estimated from the elastic recovery of Butyl rubbers in the Mooney viscometer, and the stress immediately before the rotor was released from the driving mechanism to permit the recovery to occur.

It is customary to think of E as consisting partly of the energy required to produce enough local free volume to permit the molecular movements required for flow. If the present theory is extended in this manner, and if it is assumed that E is the only parameter that varies appreciably with pressure, the free volume of activation can be computed from experimental data on the pressure coefficient of viscosity. Furthermore, if the free volume is multiplied by the internal pressure, the energy of formation of the free volume is obtained. The internal pressure can be computed from the cohesive energy density, or from the interaction constant.

On the basis of pressure coefficients of viscosity measured by Wolstenholme and Schrappel[13], some computations of this kind have been made. The computed energies of free volume formation are of the order of the heats of activation. However, these computations will not be reported, because more careful examination of all the data available indicates that some other parameters besides E are pressure sensitive also; and if they are, the computed free volume is in error. More extensive auxiliary data are necessary before this extension of the theory can be profitably pursued.

DISCUSSION

The values of E in Table I are in approximate agreement with values computed by other workers[1,12]. The values of N, which are of the order 10^{11} cm.$^{-2}$, indicate a rather low density of bonds per unit area. Thus, in the case of Hevea rubber, if a bond consists of a crystallite group of four isoprene monomer units, the cross-sectional area of the group is of the order 10^{-14} sq. cm.; and the fractional part of the interfacial area that is bonded is $1/1000$. This low value for the bonded area goes far to justify the assumption in the theory that the stress on any particular bond is strictly proportional to its age and is not appreciably affected by the rupture of a nearby bond.

The values of t_a, the mean life of a bond, are of the order 10^{-2} under the chosen conditions, $T = 100°$ C, $g = 0.2$ cm.$^{-1}$. Equations in the appendix show that as $g \to \infty$, $t_a \to$ constant $\times (\ln g)/g$. As $g \to 0$, the equations indicate that $t_a \to$ constant; but in this case the theory is not valid, because of diffusion effects.

The values of R are of the order 10^{-8}. The transmission coefficient, which is included in the factor R, should be unity, or close to it, according to the picture of the flow mechanism underlying the theory. The small value of R therefore indicates a large entropy of activation. The source of this entropy is not at all clear; but one possibility can be suggested. In the theory as it stands the spatial distribution of the heat of activation in and around the bond that is being released is not specified. However, the bond supposedly involves quite a number of atoms. Hence there may be some required spatial distribution of the energy of activation and perhaps some coordination in direction and phase of the associated thermal vibrations. The analysis of such possibilities would constitute another major step in development of the theory.

The theory as it stands yields parameter values which seem reasonable. A more severe test of the theory would be possible if data were available for both the flow and the diameters of the rheological units in a series of similar rubbers of various molecular weights.

APPENDIX

The integrals in Equations (7) and (12) can be expressed as power series in the two cases $\alpha \ll 1$ and $\alpha \gg 1$, corresponding respectively to very small g and very large g. The approximations are: for $\alpha \ll 1$, or small g,

$$
\begin{cases}
I_1 = \alpha(1 - \alpha^2 + 9\alpha^4 + \cdots) \\
I_2 = \alpha^2(1 - 4\alpha^2 + 64\alpha^4 + \cdots) \\
\rho = I_2/I_1 = \dfrac{1}{\alpha}(1 + 3\alpha^2 + \cdots)
\end{cases}
$$

and for $\alpha \gg 1$, or large g,

$$
\begin{cases}
I_1 = \ln\dfrac{1}{\epsilon} - 0.5772 + 2\epsilon - \epsilon^2\left[1.159 + \ln\dfrac{1}{\epsilon}\right] + \cdots \\
I_2 = \tfrac{1}{2}\ln^2\dfrac{1}{\epsilon} - 0.5772\ln\dfrac{1}{\epsilon} + 0.989 \\
\qquad\qquad\qquad\qquad - \epsilon^2\left[\tfrac{1}{2}\ln^2\dfrac{1}{\epsilon} + 1.571\ln\dfrac{1}{\epsilon} + 1.312\right] + \cdots \\
\rho = \tfrac{1}{2}\ln\dfrac{1}{\epsilon} + 0.1443 + \cdots \\
\epsilon = 1/(2\alpha)
\end{cases}
$$

Neither of these sets of equations is valid in the neighborhood $\alpha = 1$; and for such cases numerical integration is required.

Table II shows some computed values which are sufficient for plotting a theoretical ρ, α curve.

The foregoing approximate equations for ρ can be transformed into explicit equations for g as a function of τ, in other words explicit flow equations. It may be of interest to note that these flow equations agree in form with the linear and the exponential approximations, respectively, of the Smallwood-Eyring theory.[1] In the intermediate, transition region from small to large α, the exact equations of the new and the Smallwood theory do not agree. The

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TABLE II

THE FUNCTION $\rho(\alpha)$[a]

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α	I_1/α	I_2/α^2	ρ/α
10^{-3}	1.0	1.0	1.0
10^{-2}	0.9999	0.9996	0.9997
10^{-1}	0.9909	0.9664	0.9752

α	I_1	I_2	ρ
10^0	0.7545	0.4423	0.5862
10^1	2.508	3.721	1.484
10^2	4.731	11.97	2.529
10^3	7.025	25.49	3.628
10^4	9.326	44.31	4.751
10^5	11.63	68.44	5.885
10^6	13.93	97.87	7.025
10^7	16.23	132.6	8.168
10^8	18.54	172.6	9.313
10^9	20.84	2180.0	10.46
10^{10}	23.14	268.6	11.61

[a] For notation see Equations (7), (12), and (11).

cumulative difference in the transition region is such that if the parameters are chosen to give quantitative agreement between the two theories at high g, then for low g the g given by Smallwood is 3.56 larger than the g given by the present theory for the same τ and T.

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SUMMARY

</div>

A theory of the viscosity of raw rubbers is developed on the postulate that raw rubbers, when subjected to continuous shear in the non-Newtonian region of flow, consist of microscopic rheological units which are semipermanent aggregates of many rubber molecules[4]. The theory treats these units as tacky, elastic solids, whose relative movement and slippage constitute the macroscopic flow of the rubber. The resulting theoretical flow curve differs little from that given by Smallwood[1], but the interpretation of the parameters is radically different. The new theory leads to expressions for the number of temporary point attachments per unit area between two touching rheological units and for the mean life of these attachments.

Agreement with experimental data is slightly better than in Smallwood. Two types of observed deviation from the theory can be interpreted as due to two plausible phenomena not included in the mathematical treatment.

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THE ABSOLUTE, ENTIRELY VISCOMETRIC DETERMINATION OF THE MOLECULAR WEIGHT OF HIGH POLYMERS *

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The utility of high polymers in all fields of application depends on the average molecular weight. In general, strength, elasticity and tear resistance under sudden stress increase with the molecular weight. On the contrary, processibility and solubility decrease with increasing molecular weight. The opposing requirements for quality and economy lead to the necessity of possessing as accurate a knowledge of the molecular weight as possible, to make certain that the molecular weight of a product is adequate for the requirements of a definite application.

Normally, a simple measurement of viscosity will suffice as a test for the characterization of a definite product. The knowledge of the absolute value of the molecular weight is not required in the case where it is possible to arrange different samples in a correct series. However, in many cases a numerical knowledge of the molecular weight is desirable. In the case of the reactions of cellulose, e.g., it is often necessary to determine at what point decomposition occurs. Normally, this is not possible by means of a simple viscosity determination, since its standardization against absolute methods varies with the degree of substitution and the type of solvent. To this must be added, the causes for the occurrence of structural viscosity in solutions of linear macromolecules, which also make it necessary to determine the molecular weight for the evaluation of these high polymers.

The simple expressions *molecular weight* or *degree of polymerization* are unequivocal only in the case where all of the molecules are of equal size. In practice, however, all high polymer molecules contain molecules of very different length and possibly also of different composition. Accordingly, only the average molecular weight or the average degree of polymerization possesses practical interest.

The main difficulty in the field of molecular weight determination lies certainly in the fact that one obtains by different methods different kinds of average molecular weights. This is indeed a defect as well as an advantage insofar since, because of this, a direct comparison of measurements made on the same sample by different methods is hindered, whereas on the other hand, however, it gives an aid to the characterization of polymolecularity without going to tedious fractionation. This possibility can hardly be exploited, however, as the methods available at this time become more and more inaccurate with increasing polymolecularity.

Except for methods for the determination of end groups the various kinds of molecular weight determinations are based on the determination of some

physical property of dilute solutions and its extrapolation to zero concentration. Since the osmotic pressure method, the light scattering method, and the determination of the sedimentation equilibrium in the ultracentrifuge all rest on a thermodynamic base this extrapolation is required.   But other methods also require this extrapolation, such as those for the viscosity determination and the sedimentation velocity determination, to eliminate the effects of intermolecular interactions.   In many cases still other extrapolations must be made when one wants to come as close as possible to an absolute determination.

Consequently, in general, the known methods of molecular weight determination are based on the fact that some physical property is selected which varies with the chain length and the measurements of this physical property are extrapolated for a condition for which the possibility of complications because of unknown factors, is the least.   Furthermore, one extrapolates preferably to a condition for which the absolute value of the molecular weight can be calculated using the smallest possible number of further assumptions.

The methods resting on a thermodynamic basis, namely the osmotic, cryoscopic, ebullioscopic methods and the methods depending on vapor pressure variations become inaccurate not only because of technical reasons in connection with the measurements, perhaps because the values to be measured become too small, but also because the quantities measured are so strongly masked by a series of rheological effects, such as, e.g., the occurrence of aggregation and disaggregation, of a boundary effect and a filter effect, that one runs into basic difficulties in the evaluation of these measurements.

Staudinger[1], especially, has pointed out the relationship between viscosity and molecular weight and has given the empirically established relation[2] that the specific viscosity of solutions of equal concentration of polymer homologs is proportional to the molecular weight.   Accordingly the viscosity law is as follows:

$$\eta_{sp}/c = K_m \times M_1$$

from which one can calculate the molecular weight if K_m is known.   Since, in the field of dilute solutions, one does not obtain a constant value for η_{sp}/c, the limiting value of η_{sp}/c is used as obtained by extrapolating to zero concentration.   On the other hand it is now known[3] that this extrapolation does not correspond to the actual course of the viscosity-concentration curve.   Following the provision by Umstätter of the theoretical basis, there will be shown in this paper on the basis of experimental measurements, a method which makes it possible to determine by an absolute entirely viscometric route the molecular weights of macromolecules without special hypotheses concerning shape, rigidity and solvation.   Since the viscosity of a solution of high polymers is a function of the size of the molecule, its shape and its rigidity (interaction with the solvent) one is dealing with an equation with three unknowns.   These can be solved from the shape of the flow curve knowing three independent viscosity functions which are (a) the viscosity-temperature function, (b) the viscosity-concentration function, and (c) the viscosity-velocity gradient function.

THE DETERMINATION OF MOLECULAR WEIGHT
THROUGH RHEOLOGICAL MEASUREMENTS

The flowing of a fluid can be considered as the movement of many thin layers, lamellas of fluid, of different velocities gliding past one another.   The

smallest conceivable thickness of such a lamella is determined by the dimensions of the structural elements in the fluid.

Umstätter's calculations[4], however, have shown that in a sliding movement it is never the individual molecules which slide against each other but always units which are bigger than molecular in size, which are known as micellae. In a sliding movement these structural elements displace each other as rigid structures, during which operation they are moreover in active kinetic thermal motion.   This behavior offers the possibility of determining the dimensions of the structural elements comprising micellae or molecule coils.

The velocity gradient has the dimension of frequency and gives thus the number of the molecule coils which pass one another per unit time.   For a small velocity gradient there exists proportionality between shearing stress and velocity gradient and the fluid is accordingly in the region of η_0, the viscosity at rest. However, the larger the velocity gradient becomes, the more rapidly a coil is led by the flow past the point which another coil has just left.   Thus, the perturbation of the flow lessens and the viscosity drop becomes steeper.   When the velocity gradient has become so large that indeed a new coil is brought by the flow to a position at the time another coil vacates it, then the change of position occurs with the least possible disturbance, since in this case the position changing frequency has become equal to the characteristic frequency of the molecule coil.   The decrease in viscosity is steepest at this velocity gradient. Therewith, the inflection point in the flow curve[5] is reached.   When the velocity gradient exceeds the position changing frequency the disturbances become larger and the viscosity drop becomes smaller until proportionality between shear stress and velocity gradient prevails again, and thus the region of η_∞, the viscosity of motion is reached again.

The inflection point of the flow curve is consequently a critical point.   As the position changing frequency equals the characteristic frequency of these molecule coils at this point, the viscosity of the solution at the inflection point is a function only of the size of these molecule coils in the solution and of the viscosity of the solvent, and is therefore independent of the form and elasticity of these dissolved macromolecules, i.e., of their interaction with the solvent. In a diagram of state the inflection points of the flow curves for all concentrations lie on a straight line parallel to the abscissa.   Consequently this critical velocity gradient $\hat{G}$ becomes independent of the concentration.   It is a constant of the material the position of which depends on the molecular weight of the dissolved macromolecular substance.   Moreover, the inflection points of the flow curves for all solutions of equal concentration of a polymer-homologous series lie on a straight line parallel to the ordinate[6].   Consequently, the shear stress at the inflection point, the critical shear stress $\hat{P}$, is independent of the molecular weight.

This flow behavior of high polymer solutions offers the possibility of taking into account the structural viscosity measurements for the purpose of an absolute entirely viscometric determination of molecular weight for which Umstätter[7] has furnished the hypotheses.   In its final form the equation is as follows:

$$M = \frac{K \times \check{e}}{\hat{G}}$$

where constant K has the meaning

$$K = \frac{3\,RT\,d\ln\eta/d\ln T}{\mu}$$

The viscosity of the very dilute solutions does not differ substantially from the viscosity of the solvent so that one can, without committing an error, use the viscosity of the solvent in constant K. $\check{c}$ as the minimum of the viscosity-concentration curve represents the equivalence concentration at which the dissolved macromolecules and the solvent molecules are in equilibrium. It can be assumed that above concentration $\check{c}$, where the curve begins to turn upwards, parts of the solvent are immobilized. These solvent molecules are hindered in their mobility and build a so-called "solvate shell". The transition from non-solvated to solvated molecules happens gradually, however, so that the equivalence concentration is not indicated by a clear-cut break in the viscosity-concentration curve but is a more or less wide zone depending on the molecular weight. The larger the molecular weight, the narrower this zone becomes and the more it becomes displaced towards zero concentration. In the region of extreme dilutions the values for η_{sp}/c increase again, a fact which can only be explained by progressive uncoiling of the linear macromolecules because of the excess of solvent molecules, through which freely rotating groups become more mobile. However, when no uncoiling takes place the η_{sp}/c values decrease rapidly after going through the equilibrium zone and approach the value of the solvent. In this case, the curve traverses no minimum but a maximum, the value of which must be entered in the equation for the molecular weight determination. This phenomenon is not in contradiction to the aggregation equation, since it only requires the occurrence of a singular point, that is, a minimum or a maximum in the viscosity-concentration curve. In this connection $\check{c}$ specifies the viscosity-concentration function required for the molecular weight determination and must be determined by a careful viscosity titration.

The viscosity-temperature function of the viscosity is contained in K. $\hat{G}$, the critical velocity gradient which is independent of the concentration, facilitates the knowledge of the viscosity-velocity gradient function.

At this point it should also be mentioned that concentration $\check{c}$ is the weight concentration g./g. and μ the kinematic viscosity. If, as is often the case, g./cm.³ is given, the dynamic viscosity η has to be used.

When, therefore, constant K has once been determined for the solvent, a viscosity titration of the solution has to be carried out for the determination of $\check{c}$ and a flow curve has to be plotted at any desired concentration for the determination of the critical velocity gradient $\hat{G}$, for obtaining the absolute, entirely viscometric molecular weight value. Since the viscosity of a solution of high polymers is influenced by the size, the form, and the rigidity of the molecule it is possible to determine the absolute molecular weights solely on the basis of rheological measurements, when the three viscosity functions, which are independent of one another, are known.

This absolute, entirely viscometric molecular weight value is not in contradiction with the viscometric molecular weight determined according to Staudinger. However, the difference lies in the fact that the K_m constant derived from an absolute molecular weight determination is replaced by a material constant taken from the shape of the flow curve and the viscosity-temperature function of the solvent. Further, the uncertain limiting viscosity, extrapolated by means of approximation formulas to zero concentration, has been exchanged for the equivalence concentration with the aid of a careful viscosity titration. Consequently, the possibility, which is described here, might be the first usable method for determining the molecular weights of high polymers by an absolute, entirely viscometric route. In what follows the execution of the molecular weight determination by this method is shown by means of several examples.
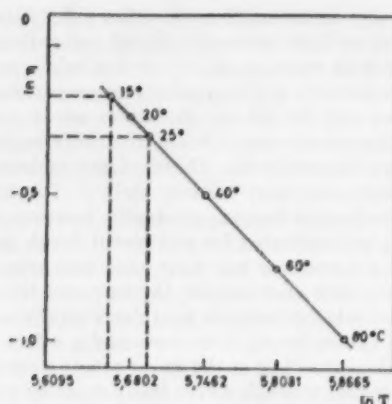
FIG. 1.—Viscosity-temperature function of butyl acetate.

EXPERIMENTAL PART

To determine the molecular weights of macromolecules in the manner indicated, the following operations are necessary:

1. The determination of the viscosity-temperature function of the solvent.
2. The viscosity titration of the solution (η_{sp} as a function of concentration).
3. The plotting of the flow curve of a solution with good structural viscosity.

The carrying out of this determination will be shown for a number of nitrated celluloses in butyl acetate, for natural rubber in toluene and for a few polyacrylonitrile preparations in dimethyl formamide.

The viscosity-temperature function.—Using butyl acetate as the solvent an example of the determination of $d \ln \eta / d \ln T$ will be demonstrated. When the natural logarithms of η are plotted against the natural logarithms of the absolute temperature (Figure 1) on normal millimeter paper one obtains almost a straight line. When using a corresponding limitation of the temperature zone between 15° and 25° C a straight line is obtained which can be differentiated graphically. Consequently $d \ln \eta / d \ln T = 4.32$ for butyl acetate. The values of $d \ln \eta / d \ln T$ for the solvents used and the calculated K constants have been tabulated in Table I. These K values are to be inserted in the molecular weight determination equation.

The viscosity-concentration function.—From what has been said it follows that the knowledge of the equivalent (with respect to configuration) concentration of the minimum or maximum of the viscosity-concentration curve $\check{c}$ is necessary. This value is obtained through a careful viscosity titration which is best carried out with Umstätter's free-flow viscosimeter[5]. In Figure 2 are plotted the titration measurements of various nitrated celluloses in butyl acetate. The

TABLE I

Solvent	$d \ln \eta / d \ln T$	K
Butyl acetate	4.32	3.05×10^{15}
Toluene	3.92	3.67×10^{15}
Dimethyl formamide	3.08	2.41×10^{15}

minimum in each case is shown by an arrow. In the same manner the curve obtained for natural rubber in toluene by viscosity titration is shown in Figure 3. The curve follows substantially the same course, for also in this case the η_{sp}/c values increase in the region of high dilutions. On the contrary, the viscosity-concentration curves shown in Figure 4 follow another course in that the η_{sp}/c values do not reach a minimum but a maximum and in the region of high dilution rapidly approach the value for the solvent. The $\check{c}$ values, obtained through
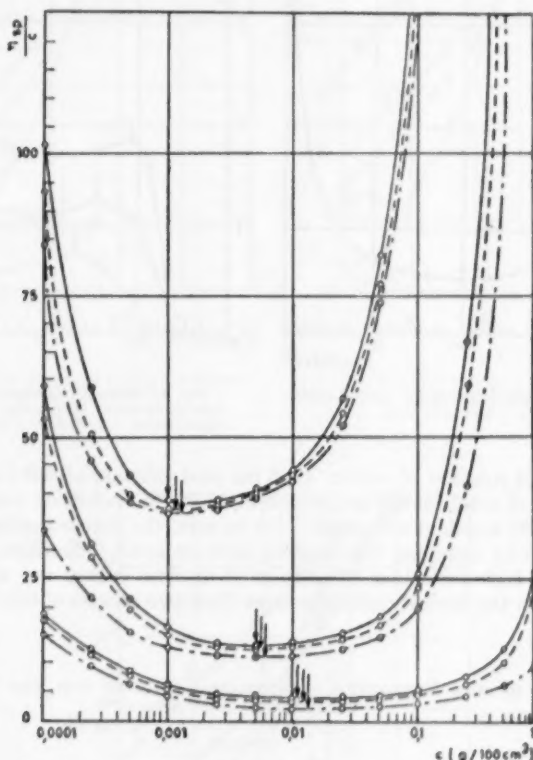
Fig. 2.—Viscosity titration of nitrated celluloses in butyl acetate, [η], respectively, from top curve to bottom = 37.3, 35.9, 34.4, 11.72, 11.25, 9.80, 4.04, 3.72, 2.98.

viscosity titration, for the substances investigated have been tabulated in Table II. These $\check{c}$ values are to be inserted in the equation used for the molecular weight determination.

Unfortunately the equivalence concentration is not shown by a sharp break in the viscosity-concentration curve, but covers rather a more or less broad zone. Therefore, the determination of the minimum by applying to the curve lines parallel to the abscissa, is somewhat uncertain and it would be desirable to use a mathematical evaluation method which permits an accurate interpolation of the minimum.

The viscosity-velocity gradient function.—In Figures 5 to 7 the flow curves for
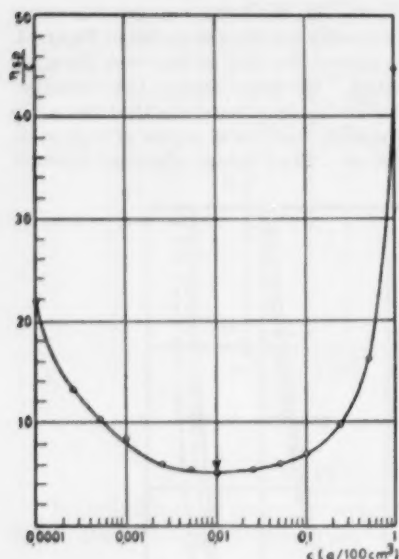
Fig. 3.—Viscosity titration for natural rubber [η] = 6.40 in toluene.
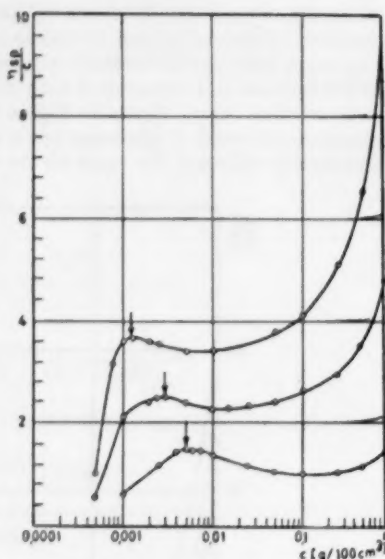
Fig. 4.—Viscosity titration for polyacrylonitrile preparations in dimethyl formamide. [η], respectively, = 2.95, 2.29, 1.04.

a 0.25 per cent solution of cotton, a 0.5 per cent solution of cellulose and 1 per cent solution of artificial silk are shown in which the inflection points with the critical velocity gradient are noted. To be sure, the determination of the correct inflection by applying the tangent presents some difficulties, particularly for the very high molecular weights as their flow curves run almost like a straight line in the critical region for more than two powers of ten. It is there-

TABLE II

THE MINIMA OF THE VISCOSITY–CONCENTRATION CURVES FOR THE INVESTIGATED SUBSTANCES IN SOLUTION

Substance	Solvent	ε g./g.
Cotton 1	Butyl acetate	1.15×10^{-5}
Cotton 2	Butyl acetate	1.26×10^{-5}
Cotton 3	Butyl acetate	1.38×10^{-5}
Cellulose 4	Butyl acetate	5.74×10^{-5}
Cellulose 5	Butyl acetate	6.31×10^{-5}
Cellulose 6	Butyl acetate	6.89×10^{-5}
Artificial silk 7	Butyl acetate	1.26×10^{-4}
Artificial silk 8	Butyl acetate	1.38×10^{-4}
Artificial silk 9	Butyl acetate	1.49×10^{-4}
Natural rubber	Toluene	1.16×10^{-4}
Polyacrylonitrile 1	Dimethyl formamide	1.2×10^{-5}
Polyacrylonitrile 2	Dimethyl formamide	3.1×10^{-5}
Polyacrylonitrile 3	Dimethyl formamide	5.17×10^{-5}
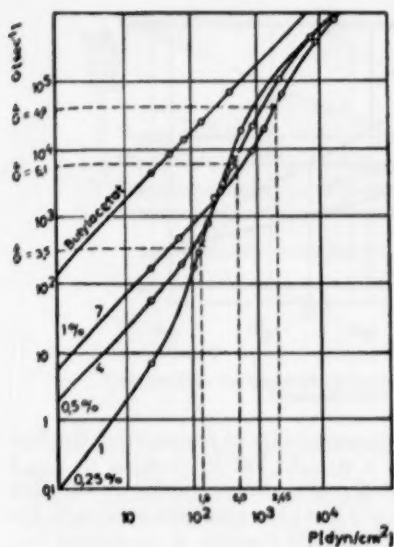
FIG. 5.—Flow curves for cotton *1*, cellulose *4* and artificial silk *7*.
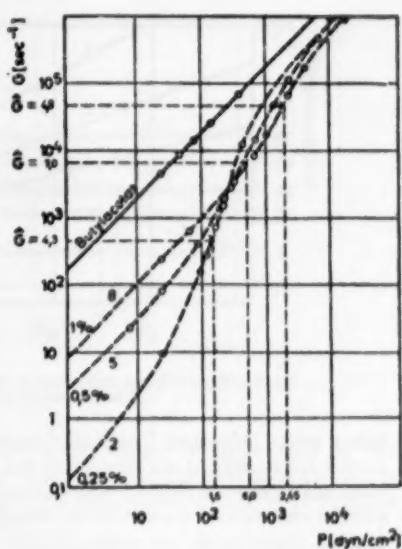
FIG. 6.—Flow curves for cotton *2*, cellulose *5* and artificial silk *7*.
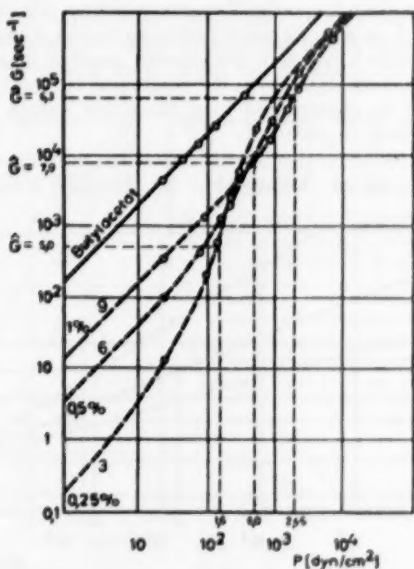
FIG. 7.—Flow curves for cotton *3*, cellulose *6* and artificial silk *9*.
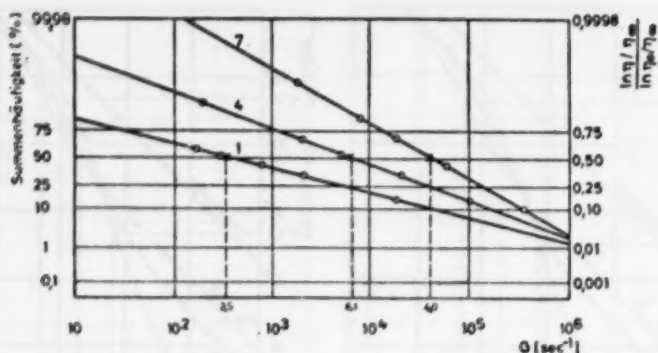
Fig. 8.—The straightened flow curves for cotton *1*, cellulose *4* and artificial silk *7*.
The ordinate is cumulative frequency.

fore a great help that Umstätter[9] found the possibility of representing the flow curves for a zone of six powers of ten by a straight line by plotting $(\ln \eta/\eta_\infty / \ln \eta_0/\eta_\infty)$ against $\ln G$ in a Gaussian cumulative probability graph. In this case η is the viscosity of a point in the structural, i.e., at low gradients zone, η_0 in the zone of viscosity at rest and η_∞ in the region of the viscosity of movement, i.e., at high gradients. The flow curves of Figures 5 to 7 drawn accordingly are shown in Figures 8 to 10 to be straight lines. In this manner the critical velocity gradient lies at the intersection of the straight line with the parallel to the abscissa at the 50 per cent point and may be read quite accurately.

The possibility of drawing the flow curves as straight lines offers moreover the great advantage that the entire flow curve can be established with about 5 measured points. A measured point in the η_0 region which can be obtained reliably with Umstätter's free-flow viscometer, another measured point in the η_∞ area and a few measured points in the structural viscous region are required. The flow curve can be constructed from these few values without having to measure the entire flow curve.

The flow curves for natural rubber in toluene at various concentrations were constructed in this manner (Figure 11). At the same time the independence
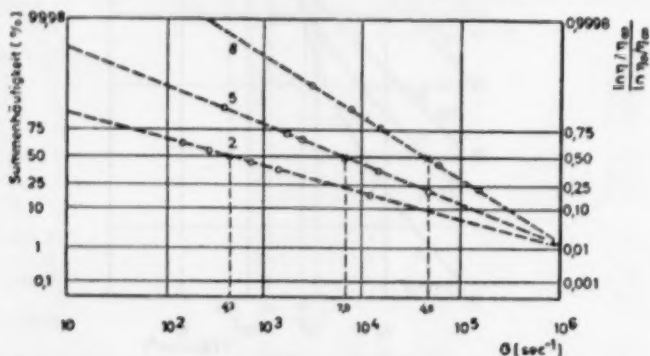
Fig. 9.—The straightened flow curves for cotton *8*, cellulose *5* and artificial silk *8*.
The ordinate is cumulative frequency.
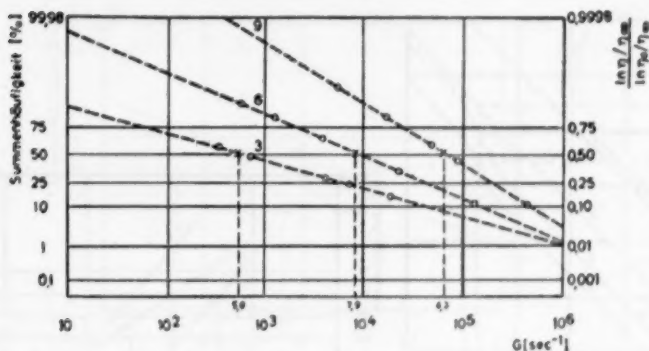
FIG. 10.—The straightened flow curves for cotton 3, cellulose 6 and artificial silk 9.
The ordinate is cumulative frequency.

of the critical velocity gradient from the concentration is made clear by this figure. If the single flow curves of the same high polymer are now plotted as straight lines (Figure 12), one finds confirmed also in this case, that all the flow curves are represented by a single curve[10].

Furthermore, the flow curves have been plotted for three different poly-acrylonitrile preparations in dimethyl formámide for the determination of the molecular weight (Figure 13). For the solutions of equal concentration of a polymer-homologous series the inflection points lie on a straight line parallel to the ordinate. The critical shear stress is therefore independent of the molecular weight. Only the critical velocity gradient is a function of the molecular weight. It is apparent from these curves that the structural viscous part of the flow curve is substantially shorter in contrast to the flow curves of the other preparations, which points to a larger homogeneity of the substances. In
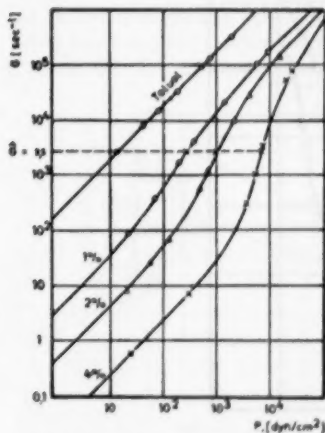
FIG. 11.—Diagram of state for natural
rubber in toluene.
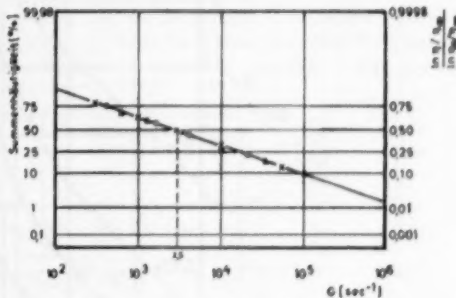
FIG. 12.—The straightened flow curves of natural
rubber in toluene. The ordinate is cumulative
frequency.
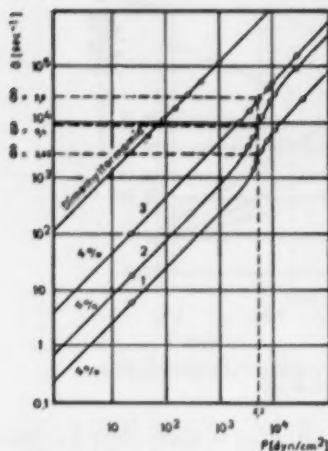
FIG. 13.—Flow curve of the polyacrylonitrile preparations in dimethyl formamide.
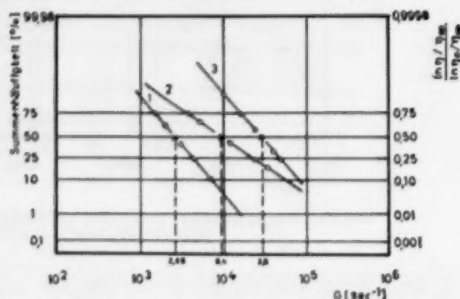
FIG. 14.—The straightened flow curves of the polyacrylonitrile preparations in dimethyl formamide. The ordinate is cumulative frequency.

Figure 14 the straightened flow curves of the same polyacrylonitrile preparations are shown also. These straight lines show a steeper inclination towards the abscissa than the straightened flow curves shown for the other preparations thus showing the greater homogeneity even more. The $\hat{G}$ values so obtained are inserted directly into the equation for the determination of the molecular weight.
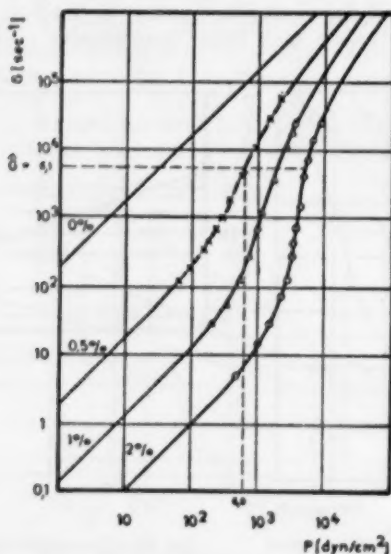
FIG. 15.—Diagram of state for a nitrated cellulose, DP = 1070, in butyl acetate.
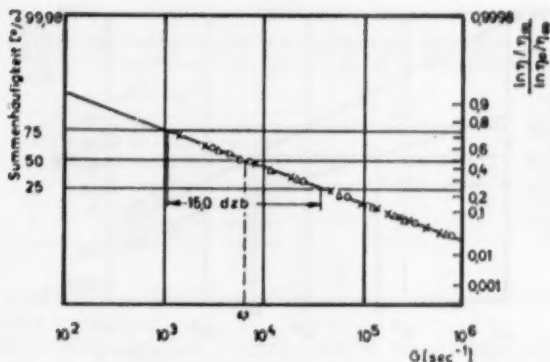
Fig. 16.—The straightened flow curves for cellulose, DP = 1070.
The ordinate is cumulative frequency.

Calculation of molecular weight and of polymolecularity.—The calculation of the molecular weight from the three viscosity functions is simple. For an unequivocal characterization of high polymers it is not sufficient to have only the statement of the average molecular weight; a knowledge of the molecular weight distribution—the polymolecularity—is also required. In what has been said previously, it has been pointed out that the polymolecularity finds expression in the flow curve. Now, the realization of the straightened flow curve offers the advantage that the inclination of this straight line in a Gaussian cumulative probability graph is a direct measure of the polymolecularity. According to a proposal by Umstätter[11] the half-value width as intersection with the parallels to the abscissa at 25 per cent and at 75 per cent is expressed in decibels (db) and thus a numerical value is obtained for the polymolecularity, without resorting to a time-consuming fractionation.

As proof for the fact that the different polymolecularity expresses itself in the inclination of the straightened flow curve, a technical cellulose (DP = 1070) has been fractionated differentially in two fractions, and the flow curve of each fraction has been plotted. Figure 15 shows a diagram made up of
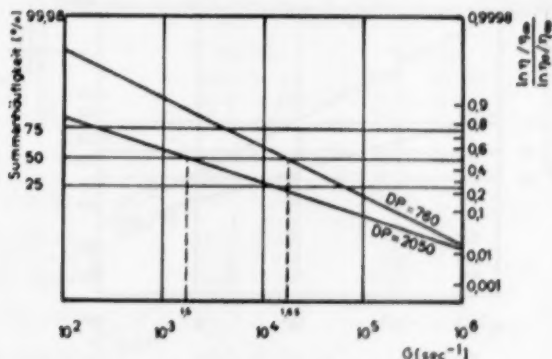
Fig. 17.—The straightened flow curves of the fractions with 80.7% low and 19.3% high molecular weight fractions of the cellulose. DP = 1070. The ordinate is cumulative frequency.
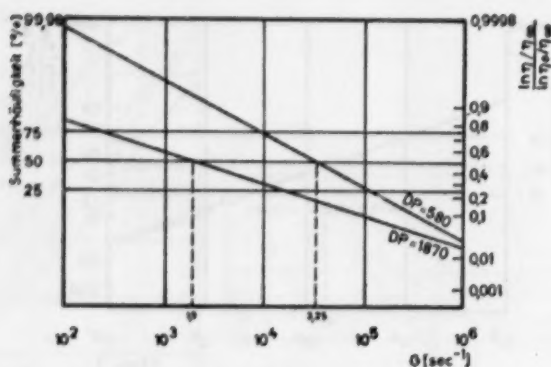
FIG. 18.—The straightened flow curves of the fractions with 59.2% low and 40.8% high molecular weight fractions of the cellulose. DP = 1070. The ordinate is cumulative frequency.

various concentrations of the unfractionated cellulose. In Figure 16, the straightened flow curves are shown in a cumulative probability graph, in which also in this case the straight lines of the different concentrations lie above one another, and therefore are represented by a single straight line. The polymolecularity amounts to 15 db. The straight lines for the 80.7 per cent low molecular weight fractions with DP = 760 and for the 19.3 per cent high molecular weight fractions with DP = 2050 are shown in Figure 17.

Figure 18 shows the straight lines for the 59.2 per cent low molecular weight fraction with DP = 580 and the 40.8 per cent high molecular weight fraction with DP = 1870. To this should also be added Figure 19 with 28.3 per cent low molecular weight fraction with DP = 190 and the 71.7 per cent high molecular weight fraction with DP = 1440. Each straight line has a different inclination and accordingly another value for the polymolecularity. The different values have been compiled in Table III and the known fact is confirmed that the high molecular weight fractions are more uniform than the low molecular weight ones. Thus, the representation of the flow curve as a straight line
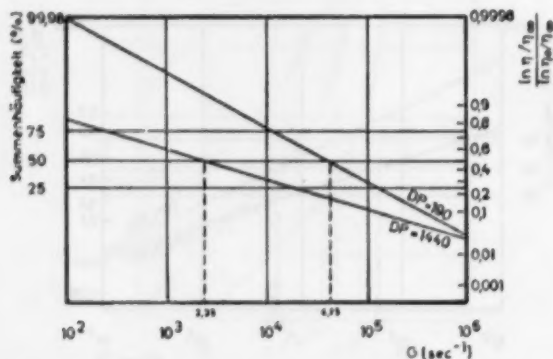
FIG. 19.—The straightened flow curves of the fractions with 28.3% low and 71.7% high molecular weight fractions of the cellulose. DP = 1070. The ordinate is cumulative frequency.

TABLE III

DEGREE OF POLYMERIZATION AND POLYMOLECULARITY OF THE
DIFFERENTIAL FRACTIONATION OF A CELLULOSE

Cellulose	DP	U in db
Unfractionated	1070	15.0
80.7% low molecular weight	760	11.5
59.2% low molecular weight	580	10.3
28.3% low molecular weight	190	10.1
71.7% low molecular weight	1440	18.3
40.8% low molecular weight	1870	17.8
19.3% low molecular weight	2050	17.5

offers the possibility of supplying information on the polymolecularity and of expressing it numerically.

In Table IV the molecular weights obtained for the high polymers investigated according to Staudinger ($M_{Staudinger}$) and the molecular weights obtained according to the absolute, entirely viscometric method described, namely, $M_{rheological}$, are contrasted with the calculated polymolecularity. When the results are compared it is found that for cellulose there is very good agreement in the molecular weights obtained by both methods. Even for natural rubber the values agree in order of magnitude. On the contrary, for the polyacrylonitrile preparations the absolute viscometric values agree only with the values obtained according to Staudinger when the maximum of the viscosity-concentration curve is inserted in the equation as $\breve{c}$ value.

The values obtained for the polymolecularity, U, from the straightened flow curves, expressed in decibels, have been compiled in Table IV. The extraordinarily small inclination of the straight lines for cotton also gives very high values for the polymolecularity whereas the somewhat more uniform composition of the celluloses show already somewhat lower values for the polymolecularity. Correspondingly, the values for artificial silk are still lower. The influence of the polymolecularity on the flow behavior stands out particularly distinctly for the polyacrylonitrile preparations. The flow curves fo· preparations *1* and *3* show only a very short structural viscous part in contrast to prep-

TABLE IV

COMPILATION OF THE MOLECULAR WEIGHTS INVESTIGATED
AND THEIR POLYMOLECULARITY

Substance	$M_{Staudinger}$	$M_{rheological}$	$U_{rheological}$
Cotton 1	95.0×10^4	100×10^4	21.1 db
Cotton 2	91.4×10^4	89.5×10^4	20.75 db
Cotton 3	87.6×10^4	84.4×10^4	19.45 db
Cellulose 4	29.8×10^4	28.7×10^4	15.0 db
Cellulose 5	28.7×10^4	27.5×10^4	14.78 db
Cellulose 6	24.9×10^4	26.6×10^4	13.1 db
Artificial silk 7	10.2×10^4	96.3×10^3	9.7 db
Artificial silk 8	95.0×10^3	87.5×10^3	9.22 db
Artificial silk 9	75.6×10^3	72.1×10^3	8.82 db
Natural rubber	14.13×10^5	16.92×10^5	15.84 db
Polyacrylonitrile 1	10.4×10^4	11.3×10^4	4.67 db
Polyacrylonitrile 2	80.8×10^3	79.5×10^3	8.05 db
Polyacrylonitrile 3	36.7×10^3	44.4×10^3	4.78 db

aration *2*. Correspondingly, the straight lines in the Gaussian summation probability graph are more or less inclined and very low values for the polymolecularity are obtained.

Therewith, it would seem that the experimentally explained method for the absolute, entirely viscometric determination of the molecular weight is the first usable method, for obtaining from purely rheological measurements, i.e., from the knowledge of three independent viscosity functions, absolute molecular weights. Although it is not so important in industry, and in practice, to obtain absolute values for the molecular weight, it should be expedient, even there, to make use of the representation by means of the straightened flow curve for the characterization of high polymers. For in this manner there is obtained at the intersection of the straight line with the parallel to the abscissa at the 50 per cent point the material constant which is a function of the molecular weight and there is obtained simultaneously a numerical representation of the polymolecularity from the inclination of the straight line.

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<div style="text-align:center">MEETING DISCUSSION</div>

NITSCHE: I believe that the method for the determination of the absolute molecular weight by the entirely viscometric route explained here is the first usable method for determining the molecular weights from rheological measurements alone. This comment should be illuminating indeed as recognition of the value of your investigations. It should also be an indication of the value that Umstätter's investigations possess. For your experimental investigations were based, as you mentioned, on his theoretical and technical (measurement techniques) preliminary investigations.

Your explanations and, particularly, the results of your investigations have also shown, however, what high demands are made now on the techniques of measurement and on him who uses such equipment. Training must keep step with the development of the technique.

ORTHMANN: A technical question: You showed in your diagrams that you have worked with concentrations of 1 mg. in 100 cm.^{3}. What flow-through times are obtained in this manner?

EDELMANN: The flow-through time in the free-flow viscosimeter is so chosen that it takes about 5–10 minutes. Then the differences in the flow-through times are sufficiently large. A mistake of 1/10 sec. would otherwise become enormous for extremely dilute solutions and would give entirely false values.

ORTHMANN: In connection with the consideration concerning error which you just mentioned: c_{min}. has rather a fairly wide course in the curve and the determination of the minimum is then always connected with a certain error. How strongly does this error reflect itself in the molecular weight? Is it ± 10 per cent or more?

EDELMANN: One can say 10 per cent.

ORTHMANN: Concerning the measured values of polyacrylonitrile: The molecular weight is composed of the two terms of the molecule inclusive of the molecular weight of the solvate shell.

EDELMANN: That is correct. We determine the solvated complex from the velocity gradient function and the temperature function of the viscosity. In order to obtain from this solely the molecular weight of the macromolecule, the value obtained for the solvated complex is multiplied by the equivalence concentration at which the macromolecule and the solvent molecules are in equilibrium.

ORTHMANN: Polyacrylonitriles are, however, more polar than the celluloses so that the solvate shell complex could be substantially greater. Is the discrepancy of the values to be attributed to this fact?

EDELMANN: Working with polyacrylonitrile is somewhat difficult. We have obtained reproducible results only after we dissolved the substance at about 80° C with a magnetic stirrer and observed a definite time for solution.

FRIND: You pointed out the upturn in the curve is particularly to be noted for the substances of high molecular weight which are structurally viscous. American investigations also attribute the upturn at low concentrations to structural viscosity. When the Couette apparatus is used this rise is not observed. Perhaps the measurement should be repeated in other equipment to see whether the rise is reproducible.

EDELMANN: In this the influence of the molecular weight on one hand and of the solvent on the other hand finds a clear expression. As polyacrylonitrile has a molecular weight of about 100,000 the rapid decrease of the η_{sp}/c values in the region of the highly diluted solutions was not to be expected. The cause might lie in the fact that polyacrylonitrile is composed of branched macromolecules.

FRIND: It would be interesting—also from the point of view of the American investigation mentioned—to check this in the Couette equipment. For terylene the minimum could be observed in another solvent. At high molecular weight the minimum became sharper but was always pushed further towards higher dilutions.

UMSTÄTTER: The question concerning the differences between the measured results in the Couette equipment and a capillary is very old. It led to differences of opinion between Ostwald and Freundlich. Originally Freundlich had believed also that there would be large differences between the measurements in the Couette apparatus and those in the capillary. They are reproduced also in W. Philipoff's "Viscosity of Colloids" (Dresden, 1942). It has been found that such differences on the whole do not exist when the sigma-phenomenon is absent. According to the investigations of Scott Blair and others—also Professor Fromm has spoken here once on this subject—there is a so-called relaxation factor. Therefore, the differences consist principally in that in a Couette apparatus we are dealing with a self-contained slot in which the fluid can be deformed as long as desired, whereas in the capillary there is naturally an end to this and the shear time is always limited. Only in the region of long relaxation periods do the curves in the Couette equipment run differently than in the capillary. There are still other differences which are connected with the distortion of the stream profile. However, this should not be the case in the region of the extremely dilute solutions.

FRIND: The American investigation has found this difference, in fact, at very low concentrations.

EDELMANN: The Couette equipment operates less accurately than the capillary viscometer by one power of ten. As in the case of the capillary viscometer the differences in the discharge times amount to only fractions of a second it is very easily possible that the upturn in the η_{sp}/c values for the very dilute solutions was not observed for the reason that the accuracy of measurement in this apparatus is entirely inadequate for catching the small differences.

UMSTÄTTER: We have discharge periods of 1000 sec. and measure even 0.03 so that only a 0.003 per cent error is involved. Such accuracy cannot be attained with the Couette apparatus according to the present state of development of the technique of measurement.

NITSCHE: An economic question: How much time do you require for the recording of a complete rheological picture for a material, including evaluation?

EDELMANN: We figure it takes a week for a determination of the absolute viscometric molecular weight including evaluation. The flow curve is recorded quickly. On the other hand the determination of viscosity-concentration function is somewhat time consuming. The preparation of the solutions and the careful cleaning of the viscometerr equire much time. Special care needs to be given also to the constancy of temperature. I believe that we could work still somewhat more quickly with Umstätter's diathermostat.

UMSTÄTTER: The structural viscosity measurements require some routine. We have not made that many measurements yet. With us the measurements with the free-flow viscometer, on the contrary, are somewhat more accurate; it is due in part to the thermostat and the time recording arrangements, etc. Really the measuring goes relatively fast. What takes more time is the preparation of the solutions. However, a week strikes me as being somewhat too long.

MELCHIOR: After one has once been convinced that the straightened curve is unconditionally reliable it would be sufficient, in general, to make two measurements, and every third and fourth measurement would only have to serve as verification.

AN INVESTIGATION OF THE MOLECULAR WEIGHT DISTRIBUTION OF POLYMERS WITH THE AID OF THE ULTRACENTRIFUGE *

S. E. Bresler and S. Y. Frenkel

INTRODUCTION

The principal parameter of polymers is the average molecular weight which can be determined osmotically, viscosimetrically, or by the method of light scattering.

However, the average molecular weight, being a statistical value, does not completely characterize a polymer, since the distribution function of molecular weight $dn/dm = q_n (M)$ (where n is the number of macromolecules and M, the molecular weight) can have infinite variety. It is known, for example, that the properties of cellulose are determined to a considerable degree by the presence of a maximum in the molecular weight distribution in the region of relatively low molecular weights (so-called hemicellulose) although the average molecular weight of the cellulose sample can be high. In the case of rubbers, the presence of low molecular weight fractions in the molecular weight distribution plays an essential role in the durability of the resulting vulcanizates. Therefore, investigation of the problem of complete molecular weight distribution of a polymer in many cases is very important. The molecular weight distribution function throws light on the mechanism of the process of the polymer formation, i.e., on the mechanism of polymerization and polycondensation reactions. It is known, for example, that the formation of a polymer is controlled by three rate constants or probabilities: k_1, the probability of active center formation which initiates the chain growth; k_2, the probability of propagation of the chain by means of addition of the monomeric unit to the end of the growing chain; and k_3, the probability of destruction of the radical which is present on the end of the growing chain. The total yield of polymer per unit time will be proportional to $k_1 L$, where L is the length of the macromolecule. On the other hand, the chain length is proportional to the value of k_2/k_3.

It is known that the radicals which are formed on the end of a growing chain can be killed in several ways: by impact and recombination, by combination with a free radical originating on decay of a polymerization initiator, or, finally, by impact with a molecule of some foreign impurity. Each process of destruction of the polymerization center has its own constant, k_3, and its average chain length L. Hence it follows that the total distribution function of a polymer can have several maxima, each of which reflects a definite mechanism of destruction of the polymerization center. This makes it possible to investigate the mechanism of polymerization in detail by determining the molecular weight distribution of the reaction product. For many years the method of fractional sedimentation has been used for investigation of molecular weight distribution in polymers. This consists of adding small portions of precipitant to a dilute

solution of a polymer.   As a result, the polymer is precipitated from the solution as a series of fractions.

Theory and experiment show, that the highest molecular weight fractions are precipitated first and the lowest molecular weight fractions are precipitated last.   By measuring the average molecular weight of the precipitated fractions and knowing their percentage yield, it is possible to build a steplike curve of sedimentation.   In building this curve, one introduces the assumption that each precipitated fraction contains macromolecules of a definite molecular weight.   It is clear that this concept cannot be true.   The theory of equilibrium solubility of the polymers predicts that the precipitated fractions should themselves have a broad molecular weight distribution.

However, the distribution function of a precipitated polymer is not determined by equilibrium solubility.   In the case of polymers, equilibrium is established very slowly and with great difficulty.   Therefore, the process of fractionation by precipitation is controlled not only by kinetic factors but also by thermodynamics though to a lesser degree by the latter.   In fractionation, rate of precipitant addition and speed of stirring as well as variation of temperature are factors which play great roles.   Therefore, if special precautions are not taken, it is impossible to reproduce fractionation of the same polymer completely and in all details.   The precipitated fractions obtained from two parallel precipitations would be different in some ways even though the amount of precipitant added were precisely the same.   All these complications forced us to be careful in handling the results obtained by the method of precipitation.

As the results of this work showed, the molecular weight distribution obtained by the method of precipitation is approximately correct, but only, in general, on a rough scale.   The fine details of molecular weight distribution are given with considerable distortion.

All that was said about the method of precipitation applies in almost the same degree to the method of fractional dissolution even in its newest modification, in which the fractions are extracted from thin films.   Thus, a question concerning an absolute method for separating fractions arises; a method which could give the same molecular weight distribution on several fractionations of the same polymer.

As will be shown later, the studies of molecular distribution of polymers with the aid of the ultracentrifuge and diffusion are free from arbitrary assumptions and permit one to get the distribution functions with a considerable degree of accuracy and confidence, although the amount of work required is considerable.

The ultracentrifuge was invented by Svedberg and was developed for determining the molecular weight of albumins, which are monodisperse substances.   For investigation of polydispersed linear polymers, the ultracentrifuge was applied by Gralen[1], Jullander[2], Kinell[3] and Ranby[4], coworkers of Svedberg.   However, the Swedish investigators did not give a method of studying the molecular weight distribution suitable for the technique of important polymers.   They confined themselves to consideration of the distribution function of polymers through the constants of sedimentation instead of the distribution function of the molecular weights.   Even this was not adequate; therefore, the problem of the molecular weight distribution function did not have its complete solution.   The ideas upon which the methods developed by us were based, were already present in the first papers of our laboratory devoted to polyamides[6].   A similar approach was taken independently of us by Baldwin and Williams[7].   However, the studies of rubberlike polymers did

force us to develop and refine considerably the methods of measurement and calculation.

BASIC PROBLEMS ARISING IN STUDIES OF THE MOLECULAR WEIGHT DISTRIBUTION WITH AN ULTRACENTRIFUGE

In development of an absolute method, we run into three basic difficulties, three essential physical problems.   In the first place, the ultracentrifuge gives us sedimentation constant distributions, but we need molecular weight distributions.   Thus, it is necessary to solve the problem of transition from sedimentation constant distributions to molecular weight distributions.   For this aim, it is necessary to determine the dependence of the sedimentation constant s on molecular weight of the polymers M.   The relationship $s = s(M)$, in the limits of one homologous series, will be quite unique.   Therefore, if the experiment gave us the distribution function of sedimentation constants of the polymer, that is $dn/ds = q_n(s)$, knowing $s = s(M)$ we could with the aid of elementary calculations find the necessary distribution function $dn/dM = q_n(M)$. The following natural way of solving the problem was contemplated.   The polymers under investigation were to be divided into the narrowest fractions possible by the method of precipitation from solution.   Then, each of these fractions was to be investigated in the ultracentrifuge.   In doing this we had to obtain not only the mean sedimentation but also the whole distribution function of sedimentation constants for each fraction.   As is known, the equation of motion for macromolecules of a certain molecular weight in the ultracentrifuge is

$$f_s \frac{d\chi}{dt} = \omega^2 \chi M (1 - V\rho) \tag{1}$$

where χ is a coordinate of a point inside of the cell (a distance from the axis of rotation); f, the molar coefficient of friction; ω, the angular velocity of the rotor of the ultracentrifuge; M, the molecular weight; V, the partial specific volume of the polymer; and ρ, the density of the solvent.   By definition the sedimentation constant is

$$s = \frac{1}{\omega^2 \chi} \frac{d\chi}{dt} = \frac{M(1 - V\rho)}{f_s} \tag{2}$$

It can be calculated from experiment by using the speed of motion of a boundary between solvent, free of polymer, and solution.   Optical methods of investigation allow measuring at each moment of time the gradient of concentration in the cell $dc/d\chi$, where c is the concentration by weight.   The accepted coordinate χ of the boundary of a sedimenting solution corresponds to a maximum value of $dc/d\chi$ (Figure 1).   During the experiment one observes the gradual motion of this maximum toward the bottom of the cell.   Using the speed of motion of this "peak", $d\chi/dt$, the sedimentation constant can be calculated.

$$s = \frac{1}{\omega^2 \chi} \frac{d\chi}{dt} = \frac{1}{\omega^2} \frac{\ln \chi_2 - \ln \chi_1}{t_2 - t_1}. \tag{3}$$

In this formula χ_1 and χ_2 are sequential positions of peaks at times t_1 and t_2.   If the sedimentation process goes correctly without any disturbance, plotting the values of $\ln \chi$ against the time function t, should give straight lines.   On

Figure 2 examples of such straight lines obtained for a series of fractions of a certain synthetic rubber are given.   Perfect linear dependence of $\ln \chi$ on t is a proof of correct operation of the sedimentation process.

In order to determine the molecular weight using the sedimentation constant, it is necessary, as follows from Formula 2, to know the values of V, ρ and f_s.   The first two can obviously by determined with the aid of the pycnometer. The molecular coefficient of friction f_s, however, is a complicated value depending on molecular weight, on hydrodynamic properties of macromolecules, on degree of coiling and penetrability for the solvent, and on concentration of the polymer.   It is clear that the value of f_s must be measured by some inde-
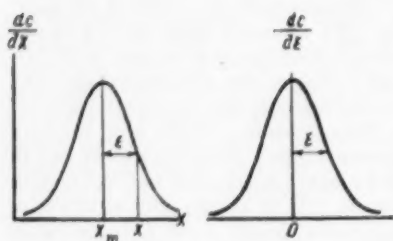
FIG. 1.—Sedimentation diagram in coordinates χ. $dc/d\chi$ and ξ, $dc/d\xi$.
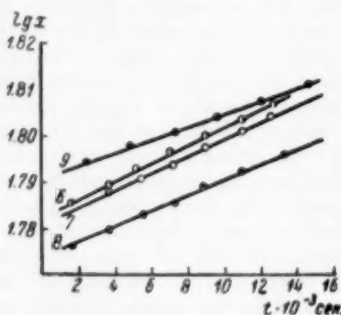
FIG. 2.—Sedimentation as function of time. The figures on the lines are numbers of fractions.

pendent method.   This can be performed by measurement of the diffusion coefficient of the polymer using some other apparatus at the same temperature and concentration of centrifuging.   As is known from statistical mechanics

$$D = \frac{RT}{f_s} \qquad (4)$$

where D is the coefficient of diffusion, and R the gas constant.

Theory and experiment show that the coefficient of friction of a molecule relative to a medium has the same value $f_s{}^s$ in the case of sedimentation and diffusion.

Thus, by measuring the diffusion constant, D, and the sedimentation constant, s, of all fractions of a polymer we can find average molecular weights of fractions using the formula

$$M = \frac{s}{D}\frac{RT}{1 - V\rho} \qquad (5)$$

Comparing these values with the values of s, we can get the function $s = s(M)$ for a homologous series which enables us to transfer from sedimentation constant dist ributions to the molecular weight distributions sought.

The second problem which has to be solved in investigating the distribution function consists of the following: It is necessary to find the molecular weight distribution using the curves $dc/d\chi = f(\chi)$ obtained from experiment for each

fraction of a polymer and by summation of the distribution curves for all fractions build the distribution function of the polymer as a whole.   The distribution function for each fraction should be calculated by comparing the curves $dc/d\chi$, obtained for each given fraction at progressive times of sedimentation.

In Figure 3 a work diagram of sedimentation is represented, Z_μ is the difference of the cathetometer readings (in microns) obtained directly from experiment by the method of superimposed scales; $Z_\mu = $ constant $dc/d\chi$ and y, the so called cell-coordinates which are counted off not from the rotation axis but from a conventional index of a cell.   The displacement along the y axis practically is equal to displacement along the x axis and conversion from y to χ can be performed using the formula $\chi = X - (Y - y)/F^{19}$ where X is a distance between the index and the rotation axis, Y, the position of the index in coordinates of the cell (or conventional reading of cathetometer assumed to be zero) and F, the photographic correction factor.   The exposure time of Curve 2 is approximately 30 minutes after beginning of the experiments and of the Curve 6, two hours; 3 and 4 are intermediate curves.
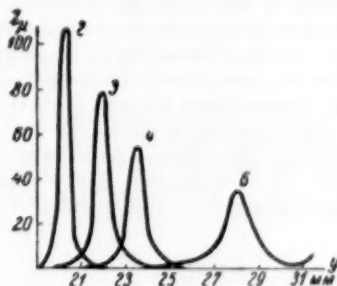
FIG. 3.—Broadening of the sedimentation boundary.   For explanation of denotations see text.

We see that the peak representing a fraction moves along the x axis and also spreads out with time.   There are two principal reasons for this broadening; diffusion of macromolecules and polymolecularity, that is, variable speed of sedimentation of different macromolecules.   This will be discussed in detail in the second section on elementary theory of border broadening.   Let us note here only that the diffusional broadening of the peaks originating independently of polymolecularity is very essential in the case of molecular weights of polymers less than 10^6.

In the papers of the Swedish authors[1-5], diffusional broadening of the peak was not taken into account and this fact introduced considerable errors in a number of cases.   The question concerning the amount of broadening caused by diffusion and by polydispersion and their separation is the second problem, which calls for solution.

The third problem is to make a correction for the dependence on concentration.   The dependence on concentration of the values s and D which one measures experimentally has not been previously mentioned.   If we go back to Formula (5) it might seem that this dependence is not essential, since in both cases it is included in the value f_s, which is excluded from the final formula.   However, this turns out to be incorrect.   In deriving Formula (4) the solution is assumed to be an ideal one.   But in the case of polymer solutions, consider-

able deviations from the osmotic equations of ideal solutions appear at concentration as low as 0.01 per cent. Consequently, in the case of polymer solutions, we are obliged to introduce a correction for the activity coefficient, beginning from very low concentrations. These corrections had to be introduced into all thermodynamic and statistical expressions. It was necessary to develop a method sufficiently simple for improving the data in connection with concentration effects.

Such were the three basic problems which had to be solved for development of the method of investigation of the molecular distribution of polymers.

ELEMENTARY THEORY OF BOUNDARY BROADENING

Usually in sedimentation experiments the observation of the motion and broadening of the boundary are performed with the aid of the refractometric method[9]. On the experimental diagram one obtains a differential distribution curve of the substance along the axis of the cell (Figure 1). Strictly speaking, the experiment gives the gradient curve of the refraction index x, $dx/d\chi$ where x is, as before, the direction in which the sedimentation is going. The specific increment of the refraction index in the limits of a homologous series is independent of molecular weight. In this case $dc/d\chi =$ constant $dx/d\chi$, and it can be assumed that the experiment gives directly the weight distribution of the polymer as a function of the distance from the axis of rotation.

The broadening of the boundary is caused by two factors: diffusion and polymolecularity. Assuming that these factors are independent[10], we can consider them separately. Let us assume, at first, that the polymer can be characterized by a homogeneous distribution function of sedimentation constants

$$q_w(s) = \frac{dw}{ds} \qquad (6)$$

(the index w means that one speaks about weight distribution; the numeric distributions in the future will be denoted by the index n) and that the diffusion is so small that it can be neglected. The constant of sedimentation, corresponding to the maximum of the sedimentation diagram χ_m, let us denote by s_m. For the symmetric distribution, $s_m = s_w$, the mean weight sedimentation constant.

According to the principal formula, Formula (3), of the method of sedimentation rate

$$\chi_m = \chi_0 e^{\omega^2 t s_m} \qquad (7)$$

where χ_0 is the meniscus coordinate; t, the elapsed time from the beginning of the experiment; and ω, the angular velocity of the rotor of the centrifuge.

The molecules characterized by another sedimentation constant, $s = s_m \pm \Delta s$ at the same moment are located at the distance of $\chi = \chi_m \pm \xi$ from the axis of rotation. By analogy with (7)

$$\chi = \chi_0 e^{\omega^2 t s} \qquad (7)'$$

Thus, the displacement ξ, which characterizes the broadening of the border, is caused by the existence of the distribution $q_w(s)$ or is the consequence of the polydispersion. Obviously

$$\xi = \chi_0 e^{\omega^2 t s_m} (e^{\mp \omega^2 t \Delta s} - 1)$$

or, going over to absolute values,

$$\xi = \chi_m (e^{\omega^2 t \Delta s} - 1) \tag{8}$$

On developing the expression in parentheses in series and persuading ourselves that we can confine ourselves to the first term (since usually $\omega^2 = 4.10^7$, $t = 10^3 - 10^4$, and $\Delta s \sim 10^{-13}$), we obtain

$$\xi = \chi_m \omega^2 t \Delta s \tag{9}$$

Assuming that χ_m is the new origin of the coordinates, let us be convinced that the sedimentation diagram or displacement distribution

$$\frac{dc}{d\xi} = q_w(\xi_s) \tag{10}$$

is quite equivalent to the initial distribution (6).   Really

$$\frac{dc}{d\xi} = \chi_m \omega^2 t \frac{dc}{ds} \tag{11}$$

but the function $dc/ds = q_w^*(s)$ coincides with exactitude up to the last multiplier with $q_w(s) = dw/ds$. Thus, the distribution function of sedimentation constants under the condition that the diffusion can be neglected, can be obtained from the sedimentation diagram with the aid of interchange of coordinates. The transfer from the abscissa χ to s can be performed using the formula

$$s = s_m \frac{\ln (\chi/\chi_0)}{\ln (\chi_m/\chi)_0} \tag{12}$$

which is derivable from (7) and (7′).

Let us normalize now the Function, (6), so that

$$\int_0^\infty q_w(s)ds = 1 \tag{13}$$

and characterize the width of this distribution by standard deviation

$$\sigma = \sqrt{m_2^0} \tag{14}$$

where

$$m_2^0 = \int_0^\infty (s - s_w)^2 q_w(s)ds$$

is the second moment of distribution about the mean[19]. The distribution $dc/d\xi$, obviously, can also be characterized by the deviation δ, which can be found from the condition

$$\delta = \tfrac{1}{2} \chi_m (e^{\omega^2 t\sigma} - e^{-\omega^2 t\sigma}) = \chi_m \, \mathrm{sh}(\omega^2 t\sigma)$$
$$= \chi_m \left[\omega^2 t\sigma + \frac{(\omega^2 t\sigma)^3}{3!} + \frac{(\omega^2 t\sigma)^5}{5!} + \cdots \right] \tag{15}$$

In general, instead of modal values of χ_m and s_m corresponding to the maximum of distribution, one should use the mean weight values χ_w and S_w. In our experiments $t \sim 10^4$, $\sigma \sim 10^{-12}$, and $\omega^2 \sim 10^7$; therefore, the series rapidly converges and it is possible to use the approximate formula

$$\delta = \chi_m \omega^2 t \sigma \tag{16}$$

All these considerations are also true in the case of distributions with several maxima, which can be considered as a sum of the simple distributions.

Let us introduce now for consideration the diffusion. It is obvious that a groups of molecules with a definite value of $s = s_i$ also has a quite definite value of the coefficient of diffusion $D = D_i$, since, in general, s and D are both (for a homologous series) simple functions of molecular weight, M. In this case the displacement distributions caused by diffusion $[q_w(\xi_D)]_i$ (Figure 4)
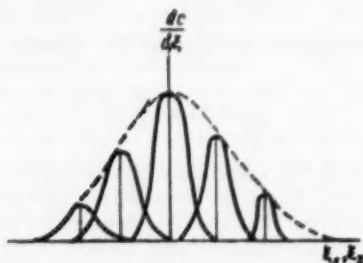
Fig. 4.—Schematic representation of broadening caused by diffusion which is superimposed on the displacement distribution caused by polydispersity.

are superimposed on the distribution of $q_w(\xi_s)$. The dotted line on the figure represents the $q_w(\xi_s)$ distribution; the solid line, $[q_w(\xi_D)]_i$, and the composite distribution turns out to be broader.

Assuming that the distribution displacement caused by polydispersity and diffusion are independent, we can write for the second moment of composite distribution

$$M_2^0 = (m_2^0)_s + \sum_{i=1}^{n} (m_2^0)_{D_i} \tag{17}$$

(theorem from the theory of probability concerning additivity of the second moments[11]).

$$(m_2^0)_{D_i} = w_i 2 D_i t \tag{18}$$

where w_i is the weight fraction of molecules with the diffusion coefficient D_i and $2D_i t$, the square of the standard deviation of the displacement distribution caused by diffusion during the time t. It is easy to see that

$$\sum_{i=1}^{n} w_i D_i = D_w$$

is equal to the mean weight coefficient of diffusion, which one usually obtains by independent measurement of D, by the method of Lamm[12]. Substituting

now into (17) the value of $(m_2{}^0)_s$ we finally obtain

$$M_2{}^0 = (\chi_m \omega^2 t \sigma)^2 + 2D_w t \tag{19}$$

It is important to note, that in our derivation the only assumption was the independence of the displacement caused by sedimentation and by diffusion. Experiments confirm this assumption[7,10,13]. We can now build up the graph for each fraction under investigation

$$\frac{M_2{}^0}{2t} = \Phi(\chi_m{}^2 t) = D_w + \frac{\omega^4 \sigma^2}{2} (\chi_m{}^2 t). \tag{20}$$

Here the value $M_2{}^0$ should be understood as the second moment of the experimental curve $dc/d\xi$. Since usually the sedimentation diagram can not be normalized to unity, one simply divides its second moment by the area and substitutes the result into (20) instead of $M_2{}^0$. The points on the graph should be situated on one straight line which cuts off on the ordinate axis a segment which is equal to D_w. The tangent of the angle formed by this straight line is equal to $\omega^4 \sigma^2/2$.

So, it was possible to achieve separation of the broadenings which are caused by polymolecularity and diffusion and to solve in general the second problem which was formulated in a preceeding section.

Until recently it was assumed on the basis of the work of Gralen[1] that if the value of the diffusion coefficient is $D \leq 10^{-6}$ cm.^{2}/sec., the portion of the diagram broadening caused by diffusion, can be neglected. Formula (19) enables us to derive a strict criterion for the resolution of this question. Let us set the condition that the standard deviation of the total distribution $q_w(\xi_{s,D})$ would exceed the standard deviation of distribution displacement caused by the polydispersity $q_w(\xi_s)$ by not more than 10 per cent.

Again, denoting $\omega^2 \chi_m \sigma t$ by δ, we get: $2Dt = \sigma^2 (1 - 0.9)^2/0.9^2$ where from: $2Dt \approx 0.25\,\sigma^2$.

Thus, if the coefficient of diffusion is determined independently and in addition to this it turns out that $2D_w t \leq 0.25 M_2{}^0$, then further treatment of the sedimentation diagram can be performed as if the broadening of the boundary had been caused by polydispersity only. In practically all important cases in which industrial polymers are studied, the diffusional broadening of the sedimentation boundary can not be neglected.

METHOD OF EQUIVALENT GAUSSIAN DISTRIBUTIONS

Up to this point we have solved the second problem of the first section only in general. We succeeded in separation of the standard deviation of displacements caused by diffusion and polydispersity, but the question concerning the distribution function $q_w(s)$ itself remained open because it cannot be determined uniquely by standard deviation. It is obvious that the broadening of the boundary is a statistical process; the probabilities of displacements ξ_s and ξ_D are determined by the distribution function $q_w(\xi_s)$ and $q_w(\xi_D)$.

Since these displacements are independent of each other, the probability of the simultaneous event is determined by the product of $q_w(\xi_s)q_w(\xi_D)$.

Obviously, the probability of the fact that the total displacement ξ will be equal to $\xi_s + \xi_D$, will turn out to be the sum of the probabilities of all particular states in which the value of ξ is disintegrated by all possible ways into the two

components ξ_s and ξ_D.   Thus, the distribution function of the total displacements $q_w(\xi)$, which we obtain from experiment, will be expressed by the following formula:

$$\frac{dc}{d\xi} = q_w(\xi) = \int\int_{-\infty}^{+\infty} q_w(\xi_s) q_w(\xi_D) d\xi_s d\xi_D \tag{21}$$

The distribution function of the displacements caused by diffusion $q_w(\xi_D)$ can nearly always be written as

$$q_w(\xi_D) = \frac{1}{\sqrt{4\pi Dt}} e^{-\xi_D{}^2/4Dt} \tag{22}$$

The second distribution function $q_w(\xi_s)$ is the quantity we are looking for.

Basically, in order to find it, it is necessary to solve the integral equation:

$$q_w(\xi) = \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{+\infty} e^{-\xi_D{}^2/4Dt} q_w(\xi_s) d\xi_D$$

From this $\xi_s = \xi - \xi_D$ and $q_w(\xi)$ is given graphically as an experimental curve.

It is possible to simplify this problem considerably and make its solution quite elementary if one introduces some physical assumptions.   Let us admit that the numerical disbribution of molecular weights within each fraction around the mean weight is random and obeys the law of error.   The basis for this assumption are the circumstances mentioned before, namely, large kinetic effects and various accidental disturbances on precipitation of the fractions.

If such hypotheses concerning the statistical distribution of the molecular weights within fractions are introduced we come immediately to the analytical expression for the distribution function of molecular weights within fractions:

$$\frac{dn}{dM} = q_n(M) = \frac{N}{\sqrt{2\pi}\mu} e^{-(\Delta M)^2/2\mu^2} \tag{23}$$

Here $\Delta M = M - \bar{M}$ is the deviation of the molecular weight from the most probable value, $\bar{M}$ (for a given fraction), N is the total number of particles and μ, the standard deviation, which, as is known in this case, must be taken into account in the distribution function.

The method based on this assumption we will call the method of equivalent Gaussian distribution.   Certainly, the introduction of the universal analytical expression for the molecular weight distribution function within a fraction and also of the expression which depends on one parameter, μ, allows considerable simplification to be made in the mathematical solution of the problem.

However, the most important factor is not the simplification but the physical fairness of the assumption made, and this can be verified by comparing various consequences of the theory with the experimental results.   Assuming Gaussian distribution within a fraction, we can immediately prove a series of important theorems.

Theorem 1.—If the molecular weight distribution within a fraction is Gaussian and the standard deviation μ is small (μ is at least four times smaller than the most probable weight M) then the sedimentation constant distribution, diffusion constant distribution, displacement distribution, etc., will also be

Gaussian for each fraction.   The function $q_n(s)$ will be expressed (23) by a given $q_n(M)$ according to the obvious formula

$$q_n(s) = \frac{dn}{ds} = \frac{dn}{dM} \Big/ \frac{ds}{dM}$$

Before, it was noted that the sedimentation constant in the limits of a homologous series is related to molecular weight by the single value function $s = s(M)$. We can quite rightfully develop this function into a series in the neighborhood of the most probable value of molecular weight $\bar{M}$,

$$s(M) = s(\bar{M}) + \Delta M \left(\frac{ds}{dM} \right)_M + \frac{(\Delta M)^2}{2!} \left(\frac{d^2s}{dM^2} \right)_{\bar{M}} + \cdots, \qquad (24)$$

where as before $\Delta M = M - \bar{M}$.   It is known, that 96 per cent of the whole area enveloped by a Gaussian curve is enclosed in the range of two standard deviations.   If, as we assumed before, $\mu \leqslant 0.25M$, then we can neglect all the members of the series development except the first two with an accuracy of a few per cent.   Doing this we get;

$$s(M) - s(\bar{M}) = \Delta s = \Delta M \left(\frac{ds}{dM} \right)_{\bar{M}} \qquad (25)$$

from which, with an accuracy up to small values of the second order

$$q_n(s) = \frac{dn}{ds} = \frac{1}{\sqrt{2\pi}\,\mu\,\frac{ds}{dM}} e^{-\frac{(\Delta s)^2}{2\mu^2 \left(\frac{ds}{dM} \right)^2_{\bar{M}}}} \simeq \frac{\exp\left[-\frac{(\Delta s)^2}{2\mu^2 \left(\frac{ds}{dM} \right)^2_{\bar{M}}} \right]}{\sqrt{2\pi}\,\mu\,\left(\frac{ds}{dM} \right)_{\bar{M}}}$$

This is true because it is possible to neglect the variation of the preexponential multiplier in the comparison with the variation of the exponential multiplier.

Introducing a new parameter $\sigma = \mu(ds/dM)_{\bar{M}}$, the standard deviation of the sedimentation constant Gaussian distribution, we finally obtain

$$q_n(s) = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-(\Delta s)^2/2\sigma^2} \qquad (26)$$

From the Gaussian distribution of sedimentation constants the Gaussian distribution of the displacements ξ_s immediately follows.   Expressing Δs by ξ_s (9) and remembering (16) that $\sigma = \delta/\omega^2 t \chi_m$, we obtain

$$q_n(\xi_s) = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-\xi_s^2/2\delta^2} \qquad (27)$$

Analogously, it can be proved that the diffusion coefficient distribution within the fraction must be Gaussian

$$\frac{dn}{dD} = \frac{1}{\sqrt{2\pi}\,\theta} e^{-(\Delta D)^2/2\theta^2} \qquad (28)$$

Theorem 2.—If the fractions satisfy the conditions set above, or, in other words, are Gaussian with sufficiently small standard deviations, then all the average weights for these fractions must coincide independently of the method of their determination. From elementary statistical consideration it follows that a number average weight $M_n = \int M dn / \int dn$, determined by the osmotic method or by determination of terminal groups, coincides with the most probable weight $M_n = \widehat{M}$.

For an average weight obtained by measurement of scattered light, we get

$$M_w = \frac{\int M^2 dn}{\int M dn} = \frac{\int M dc}{\int dc} = \widehat{M} \left(1 + \frac{\mu^2}{\widehat{M}^2} \right) \tag{29}$$

Even in the cases where $\mu = 0.3\widehat{M}$, the difference between the weights M_n and M_w does not amount to 10 per cent.

The viscosimetric average molecular weight M_n is situated between M_n and M_w[14]. Therefore, it should also practically coincide with the two previous average weights. An important consequence of this theorem is the fact, that the mode value of the molecular weight in the weight distribution

$$q_w(M) = M q_n(M) = \frac{M}{\sqrt{2\pi}\mu} e^{-(\Delta M)^2 / 2\mu^2}$$

turns out to be exactly equal to the average weight which is easy to verify by direct calculation

$$M_m = \widehat{M} \left(1 + \frac{\mu^2}{\widehat{M}^2} \right) = M_w \tag{30}$$

where M_m is the mode value (corresponding to the maximum of distribution). The coincidence of mode and average values, generally speaking, is a sign of symmetry of distribution. Since in a given case the weight distribution differs from the Gaussian weight only by the slowly increasing preexponential multiplier M, we can practically see that the multiplication of the exponential multiplier by M will result in displacement of the whole distribution along the molecular weight axis toward the larger weights by the value of $\delta M = \mu^2/M$. In fact, for the distribution $q_w(M)$ of a narrow fraction we can substitute the equivalent Gaussian distribution in the vicinity of the weight M_m. Thus, we come to Theorem 3.

Theorem 3.—In the first approximation not only number average but also weight average distributions of molecular weights, sedimentation constants, diffusion constants, displacements, etc., must be Gaussian having the same values of standard deviations as in the case of number average distribution. Only in the cases, when the fraction under consideration is itself a low molecular weight, that is, its average weight has a small value, is it possible to make an appreciable error by admitting for the weight distribution the uncorrected Function

$$\frac{dc}{dM} = \frac{\widehat{M}}{\sqrt{2\pi}\mu} e^{-(\Delta M)^2 / 2\mu^2} \tag{31}$$

In the case of rubber fractions with average molecular weights lower than 100,000 we used the complete expression:

$$\frac{dc}{dM} = \frac{M}{\sqrt{2\pi\mu}} \, e^{-(\Delta M)^2/2\mu^2} \tag{32}$$

which in the given case ($\bar{M}$ and μ of the same order of magnitude) differs notably from the Gaussian function.

Theorem 4.—The experimental curves which represent the distribution functions of displacements $q_w(\xi)$, are also Gaussian ones. This conclusion, which follows from the general theorems of the theory of probability, can be obtained by direct substitution of $q_w(\xi_s)$ and $q_w(\xi_D)$ in Equation (21). Thus:

$$q_w(\xi) = \frac{\text{const}}{\sqrt{2\pi} \, \overline{\xi^2}} \, e^{-\xi^2/2\overline{\xi^2}} \tag{33}$$

where

$$\overline{\xi^2} = \delta^2 + 2Dt$$

This circumstance considerably simplifies the calculation of the second moment of the sedimentation diagram which turns out to be

$$M_2^0 = \frac{F^2}{2\pi H^2} = \overline{\xi^2} \tag{34}$$

where F is the area, and H, the maximal ordinate of the sedimentation diagram. The values so obtained should be substituted into (20) and separation of the broadenings caused by polymolecularity and by diffusion performed. If the diffusion coefficient was measured independently, the standard deviation σ can be calculated immediately using the formula

$$\sigma = \left(\frac{\overline{\xi^2} - 2Dt}{\omega^4 \chi_m^2 t^2} \right)^{\!\frac{1}{2}} \tag{35}$$

The coincidence of the diffusion coefficient which was determined independently with the value of $(\overline{\xi^2}/2t)_{t=0}$ is an additional proof that a fraction is Gaussian.

Now the second problem of the first section is completely solved. For each fraction of the polymer one finds the distribution function using the sedimentation constants;

$$q_{w_i}(s) = \frac{dw_i}{ds} = \frac{w_i}{\sqrt{2\pi\sigma_i}} \, e^{-(\Delta s)^2/2\sigma_i^2} \, ; \quad \Delta s = s - s_i$$

where s_i is the average value of s for the ith fraction, and σ_i, its standard deviation. Then, on a plot, one builds the Gaussian curves which correspond to all fractions into which the polymer was divided. Each curve should be normalized so that its area would be proportional (or equal if the corresponding scale was chosen) to the weight part, w_i, of a given fraction relative to the total weight of the polymer, which is assumed to be unity.

Graphic summation of the distribution functions for all fractions will give

the total sedimentation constant distribution function of a polymer. Examples of such plotting will be given in the next paper.

COMPARISON WITH EXPERIMENT

All principal consequences of the theory developed in the previous section were experimentally examined.

1. The simplest conclusion of the theory is that the experimental curves themselves, which were obtained in the ultracentrifuge and represented the distribution function of the displacements $q_w(\xi)$, have to closely approximate
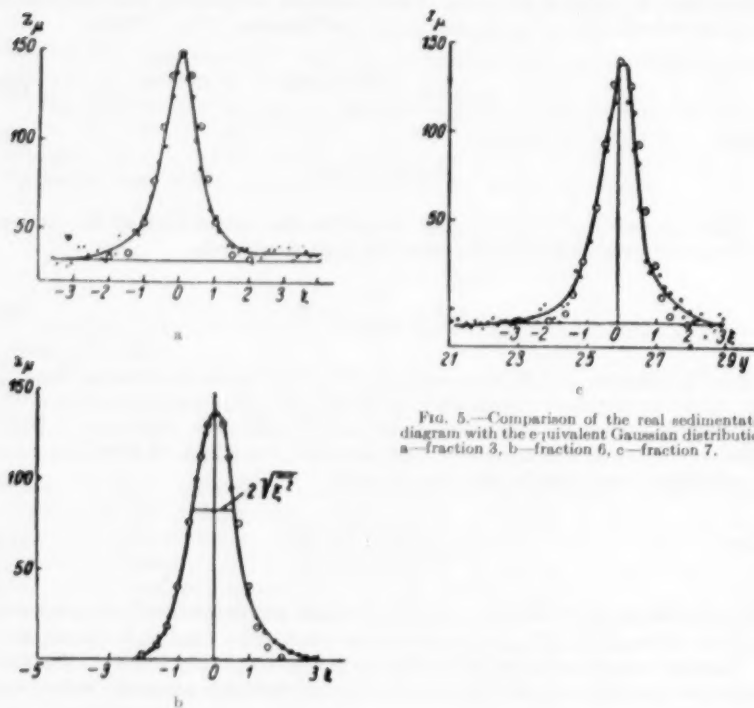
FIG. 5.—Comparison of the real sedimentation diagram with the equivalent Gaussian distribution; a—fraction 3, b—fraction 6, c—fraction 7.

Gaussian curves. Figure 5 gives the experimental curves for a series of fractions from one rubber. On the curves are placed the points of Gaussian functions which give the closest interpretation of the experimental data. We can see that the coincidence is quite satisfactory.

2. Formula (34) of the previous section enables us to examine the theory by independent means. Really, plotting the values $\bar{\xi}^2/2t$ belonging to the same fraction for a series of successive moments of time, as a function of the argument $\chi_m^2 t$, we must obtain a straight line with the initial ordinate equal to D_w. Figure 6 represents the straight lines for the series of fractions (1–5) obtained from experiment. On the ordinate axis are denoted the points D_w which are determined in an independent way. We are convinced that in most cases the

theory is excellently borne out by experiment.   The values of the diffusion coefficients directly measured and obtained from sedimentation diagrams turn out to be equal.

3. The third and most important conclusion from the theory, formulated in Theorem 2, is the equality of various average molecular weights of a given fraction.   Figure 7 illustrates the correctness of this rule.   On the ordinate axis are plotted the values of logarithms of the sedimentation constants of various fractions as a function of logarithms of molecular weights measured by various methods (concerning the choice of coordinates, see the next section).   We can see that the points which correspond to all fractions of the same synthetic rubber fall closely on a straight line.   Evidently the variation of the molecular weights for the same fractions determined by various methods of measurement are in the range of accuracy of the measurements.

The experiments do not show any systematic deviation from the predicted relationship.
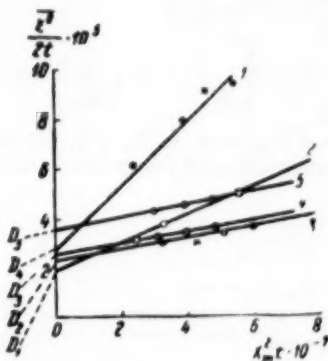
FIG. 6.—Graphic separation of displacement caused by polydispersity and diffusion.
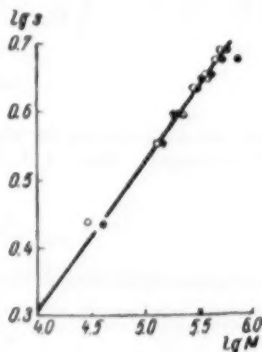
FIG. 7.—Coincidence of various mean molecular weights.   Asterisks —M_z; rings—M_η, M_n; dots—M_w.

TRANSITION TO MOLECULAR WEIGHT DISTRIBUTION

As was indicated above, for transition from distribution function of sedimentation constants to the distribution function of molecular weights it is necessary to know the character of the relationship between s and M.

$$\frac{dw}{dM} = q_w(M) = q_w(s) \frac{ds}{dM} \tag{36}$$

According to the Debye-Bueche theory[15]:

$$s = AM^{1-\alpha} \tag{37}$$

where A is a constant characteristic of the system polymer-solvent, and α, a parameter of the penetrability of the molecular conglomerates.   At $\alpha = 1$, the molecules are completely transparent for the solvent but at $\alpha = 0.5$, the conglomerates are impenetrable.   For most of the polymers investigated α does

not exceed 0.7. Thus

$$q_w(M) = q_w(s)(1 - \alpha)\frac{s}{M} \tag{38}$$

From this it follows that the ultracentrifuge resolves the molecular spectrum of compact molecules considerably better than semipenetrable conglomerates. At $\alpha = 1$ the sedimentation constant is no longer dependent on the molecular weight.

Let us characterize now the $q_w(M)$ distribution within a narrow fraction by means of the standard deviation μ and try to find the relationship between σ and μ[14]. Analogously with (15) it is necessary to assume that

$$\sigma = \varphi(\mu) = \tfrac{1}{2} A[(M_w + \mu)^{1-\alpha} - (M_w - \mu)^{1-\alpha}] \tag{39}$$

where M_w is the mean weight. From this we find

$$\sigma = A M_w^{1-\alpha}\left[(1 - \alpha)\left(\frac{\mu}{M_w}\right) + \frac{(1 - \alpha)\alpha(1 + \alpha)}{3!}\left(\frac{\mu}{M_w}\right)^3 \right.$$
$$\left. + \frac{(1 - \alpha)\cdots(3 + \alpha)}{5!}\left(\frac{\mu}{M_w}\right)^5 + \cdots\right]$$

Since in the distributions for the fractions of a polymer $\mu/M_w \leqslant 1$, this series rapidly converges. Since $A M_w^{1-\alpha} = s_w$, with a sufficient degree of accuracy:

$$\sigma = \frac{s_w}{M_w}(1 - \alpha)\mu \tag{40}$$

then for symmetrical distributions $(M_w = M_m; s_w = s_m)$

$$\sigma = \frac{s_m}{M_m}(1 - \alpha)\mu \tag{40'}$$

So we get in general the same relationships which were previously derived specially for Gaussian distributions [see Formula (26) or (25)]. According to (37),

$$\left(\frac{ds}{dM}\right)_{M_m} = (1 - \alpha)\frac{s_m}{M_m}$$

The parameter α can be found from the slope of straight lines of the type given in Figure 7.

The second paper will show that this parameter increases with concentration at the concentration at which the experiments were performed. It is understandable that in calculations the real values of α should be used, instead of that which will be obtained on extrapolation to infinite dilution

CORRECTION OF DEPENDENCE OF s AND D ON CONCENTRATION

The concentration of the polymer enters the value s_m, the sedimentation constant, through the molar coefficient of friction $f_0(c)$

$$s = \frac{M(1 - \nu\rho)}{f_s(c)}$$

As the concentration c is decreased, the value of s increases hyperbolically. Therefore, many authors express the realtionship between s and c by an empirical equation

$$s = \frac{s_0}{1 + k_s c} \tag{41}$$

or, by the quite equivalent expression

$$f_s = f_s{}^0(1 + k_s c)$$

The values s^0 and $f_s{}^0$ correspond to infinitely dilute solutions. Our data also can be well described by Formula (41); this is evident in Figure 8, where $1/s$ is given as a function of c for two rubber fractions.
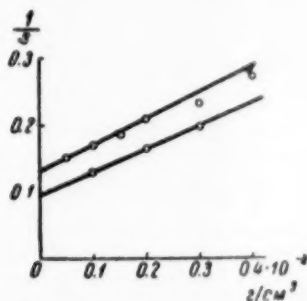
FIG. 8.—Dependence of the sedimentation constant on concentration (the method of extrapolation to infinite dilutions, according to Gralen) Upper curve, K-1, fraction 2; Lower, K-3, fraction 3.

Let us consider now the dependence of diffusion on concentration. In the diffusion coefficient the same value f_s with its dependence on concentration enters, but in addition diffusion is very much dependent on nonideality of the polymer solution. It is known that solutions of polymers at a concentration of several hundredths of a per cent already deviate considerably from the law of ideal solutions $\pi/c = RT/M$ (here π is osmotic pressure, R, the gas constant, M, molecular weight, and c, the concentration in g/cm.^{3}).

The interaction between macromolecules in real solutions can be accounted for by introduction into the osmotic equation virial coefficients which characterize double, triple, etc., types of interaction to give

$$\frac{\pi}{c} = RT \left(\frac{1}{M} + B_2 c + B_3 c^2 + \cdots \right) \tag{42}$$

Usually at small concentrations it is possible to confine ourselves to the second member of the series development. The second virial coefficient B_2 in the first approximation is weakly dependent on molecular weight. In a narrow range of variation of M, this dependence can be neglected and we can assume that B_2 is a constant value for a series of homologous fractions. By introduction of the thermodynamic activity correction[16,17] we get for the diffusion coefficient

instead of Equation (4) the corrected formula

$$D = \frac{RT}{f_s(c)} (1 + 2B_2cM) = \frac{RT}{f_s^0} \frac{1 + 2B_2cM}{1 + k_sc} \tag{43}$$

The second virial coefficient can be found from experiment by osmotic measurements, but the most convenient way is light scattering measurement. If τ denotes extinction caused by light scattering (so called turbidity) H, the optical Debye constant[18],

$$H = \frac{32\pi^3}{3\lambda^4} \frac{\chi_0^2}{N} \left(\frac{\Delta\chi}{c} \right)^2,$$

where λ is the light wave length, N, Avagadro's number, χ_0^4, refractive index of the solvent, $\Delta\chi$, increment of the refractive index of dissolved polymer, and c, the concentration in g./cm.[3], then;

$$\frac{Hc}{\tau} = \frac{1}{M} + 2B_2c \tag{44}$$

In Figure 9 are presented the straight lines obtained by us for Hc/τ as a function of c for a series of fractions of the synthetic rubber. We see, that in the range of a tenfold variation of the molecular weight, the second virial coefficient does not depend on M. Therefore the correction of B can be performed using measurements on unfractionated samples of polymer.

If the activity correction is introduced into the diffusion coefficient, we can neglect the dependence of f_s on concentration, because on calculation of molecular weights the value of f_s cancels out. Thus, direct calculation using Svedberg's Formula (5) at a finite concentration leads to the "apparent molecular weight" M_c, which is dependent on concentration.

$$M_c = \frac{sRT}{D(1 - V\rho)} = \frac{M}{1 + 2B_2cM}$$

Fig. 9.—Determination of second virial coefficient from light scattering experiment.
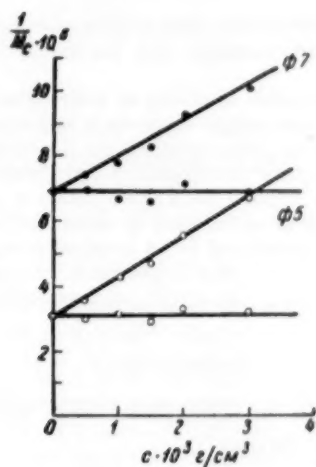
FIG. 10.—Verification of Formula (45) for true molecular weight.   On the ordinate axis the reverse values of M_m and M_c are plotted, since in this case the dependence of M_c on concentration can be expressed by a straight line with the slope $2B$ $(1/M_c) = (1/M) + 2B_c$.

The true molecular weight can be figured out using the formula

$$M = \frac{M_c}{1 - 2B_2 c M_c} \tag{45}$$

The width of the sedimentation peak also is dependent on concentration. However, the transfer from the distribution function of sedimentation constants to the distribution function of molecular weights is performed with the aid of the empirical formula, $s = A M^{1-\alpha}$, which is found at the same concentration, c, at which the measurements were carried out.   Actually the calculation is performed using the formula $\mu/M_m = (1 - \alpha)^{-1}(\sigma/s_m)$.   It is clear that the values μ and M_m in this formula cannot depend on concentration.

In practice it is necessary to take into account the variation of concentration along the sedimentation boundary.   This leads to a sort of under compensation of the effect of concentration in calculations using Formula (40′).   Experiment shows, however, that the inaccuracy admitted by this is insignificant.

In Figure 10 are given the results of experiments made with two fractions of synthetic rubber for verification of Formula (45).   The values of s_m and D were determined at different concentrations and using them the apparent weight was calculated.   Then, using Formula (45) the true molecular weight was calculated.   From Figure 10 it is evident that the true weight really does not depend on concentration, that is to say, the method of correction of the data introduced by us is quite valid.   An analogous method was independently arrived at by Schulz[16].

CONCLUSIONS

In the present paper a method for studying the molecular weight distribution of linear polymers, involving the following stages, is developed:

1. Fractionation of the polymer into a series of sufficiently narrow fractions and investigation of these fractions with the aid of the ultracentrifuge and diffusion.

2. Plotting the distribution functions of sedimentation constants for each fraction and subsequent summation of curves in order to build up the distribution function of the sedimentation constants for the whole polymer.

3. Discovery of a general functional relation between the sedimentation constants and molecular weights for a given series of polymer homologs and construction of the distribution function of molecular weights of the polymer. The basis of the method developed by us (method of equivalent Gaussian distributions) was confirmed by direct experiment. Application of this method of investigation to a number of industrial polymers will be described in the next paper.

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19 Translator's note: In the equation given S_0 is probably an error and should be S_m.

THE INVESTIGATION OF MOLECULAR-WEIGHT DISTRIBUTION IN RUBBERLIKE POLYMERS *

S. E. BRESLER, I. Y. PODDUBNYI, AND S. Y. FRENKEL

INTRODUCTION

In the investigation of the properties of rubberlike polymers, it is very important to find the molecular-weight distribution function. Among known methods of molecular weight determination, only the ultracentrifuge method makes possible the determination of both the average value of the molecular weight and the molecular-weight distribution function.

In the previous paper[1], it was shown how this problem can be completely solved. Usually, in order to trace the distribution curve, the sample is separated into a series of fractions, a method which is based on the relationship of critical conditions of the solubility of the polymer to the molecular weight.

The possibility of obtaining relatively homogeneous fractions by the method of precipitation from solutions had not been proved experimentally until now, and the opinion that the distribution within each fraction is identical with that of the starting polymer had not even been expressed. Therefore, the question of the degree of authenticity of the distribution function obtained by graphic differentiation of the integral curves of precipitation[2] remained unsettled.

The problems of this investigation were: (1) application of the method of investigation of linear polymers with the aid of the ultracentrifuge developed in our laboratory to several rubberlike polymers; (2) determining their molecular-weight distribution function; (3) comparing this distribution function with that obtained by graphic differentiation of the integral curve of precipitation; and finally, (4) estimating, because of its interest, the molecular-weight distribution of those fractions which were obtained by fractional precipitation from solution.

For this investigation two samples of diene rubber whose Karrer plasticity values were 0.3 (sample K-1) and 0.26 (sample K-3) were selected. Another sample of relatively low molecular-weight Buna-S whose Karrer plasticity was 0.5 was also used (sample K-2).

FRACTIONATION OF THE POLYMERS

Fractionation of the rubbers was performed by fractional precipitation from benzene solution, using methyl alcohol as the precipitant.

In the method used, which has been described in a general way by Zhukov, Poddubnyi and Lebedev[3], the conditions of effective fractionation which are the consequence of a thermodynamical consideration of the fractionation process were taken into account[4]. The fractions were precipitated from 0.9–1 per cent solutions. After decantation of the solutions, they were redissolved and reprecipitated from 0.3–0.4 per cent solutions.

It is known that the rubber fractions of highest molecular weight partially lose their solubility during the drying process. Because of this fact, drying of the precipitated fractions was avoided. Each precipitated fraction was dissolved directly after washing in one liter of benzene, and the resultant benzene-methanol azeotrope was distilled off under reduced pressure at 30° C until the methanol was completely removed. The refractive index of the distillate was used as a measure of the completeness of removal of the methanol.

The quantity of rubber in each fraction was determined by concentration of a given volume and weighing the residue after vacuum drying.

TABLE I

Polymer	No. of fraction	Weight of fraction	Osmotic molecular weight $M_n \times 10^{-3}$	Viscometric molecular weight $M_n \times 10^{-3}$	Mean molecular weight* $M_w \times 10^{-3}$
	1	0.0701		525	600
	2	0.1009		496	525
	3	0.1021		382	
K-1	4	0.1486		363	347
	5	0.1582		299	
	6	0.1484		219	212
	7	0.1311		138	
	8	0.1406		32	
	1	0.0800	325		
	2	0.1169		316	
	3	0.1054	188		
	4	0.1025		140	
K-2	5	0.1131	100		
	6	0.1942	68		
	7	0.0681	53		
	8	0.1266		36	
	9	0.0865		20	
	1	0.032	953	922	
	2	0.063		876	
	3	0.059	636	691	
	4	0.088		556	
	5	0.061	459	462	
	6	0.075		451	
K-3	7	0.105		371	
	8	0.078		331	
	9	0.114	302	298	
	10	0.087		246	
	11	0.099	190	188	
	12	0.139	101	100	

* By light scattering data.

The results of fractionation of the rubber samples investigated are given in Table I. The molecular weights of the samples were determined by osmometric and viscometric methods. In the case of four fractions of K-1 the light-scattering method was applied. The viscometric molecular weights of fractions were computed on the basis of viscosity data and relationships of the type:

$$[\eta] = \phi(M)$$

These were obtained for each sample of rubber used. Evaluation of the constant ϕ was made according to the mean value of osmometric molecular weight. Determination of the true molecular weight by the ultracentrifuge method

and diffusion was one of the aims of this investigation and the results will be given below. The tracing of the molecular weight distribution curves was carried out in the usual way. For this purpose the integral weights were plotted against the molecular weights, the data being taken from Table I. The resultant steplike graphs were smoothed to give the distribution curves of integral weights.

Using the method of graphic differentiation, the differential molecular-weight distribution curve was obtained. These curves are given in Figures 11 and 12 as dotted lines.

It is necessary to point out the following experimental details. It was found that sample K-3 was extremely sensitive to oxidation. The viscosity of a solution of this polymer decreased remarkably within one to two days when no special precautions were taken. We were able to avoid this difficulty by:

1. Carefully degassing the solvents by blowing nitrogen through them while refluxing.
2. Performing all fractionating operations under nitrogen.
3. Adding 1–2 per cent, based on the rubber, of an antioxidant (phenyl-2-naphthylamine), to the rubber solutions.

For measuring the constants of sedimentation and diffusion, we used octane (K-1 and K-3), cyclohexane, and cyclohexene (K-2) as solvents. The choice of solvents was governed by two requirements:

(1) The solvent had to have a refractive index as different as possible from that of the polymer.
(2) The density of the solvent and the polymer had to be as different as possible.

The other consideration, solubility of the polymer, in conjunction with the first two, limited drastically the choice of solvents.

After fractionation and purification, the fractions were obtained as benzene solutions. Since benzene is positively not suitable as a solvent for an investigation of sedimentation and diffusion, we substituted octane or cyclohexane for it. This substitution of the solvent was not performed by drying because it can result in loss of solubility (see above) but by repeated addition of large portions of new solvent to the saturated benzene solution of rubber and concentration of this solution in vacuo at room temperature.

Usually it was adequate to add new solvent to the solution and evaporate it in vacuo three times to remove practically all traces of benzene.

METHODS OF INVESTIGATION AND FORMULAS FOR CALCULATION

The sedimentation constant s in the principal series of measurements was determined with the help of an oil ultracentrifuge[5] at 60,000 rpm. The initial concentrations were: 2×10^{-3} g./cc. for K-1 and K-3 and 2.45×10^{-3} g./cc. for K-2.

Additional measurements were made at smaller concentration and lower speed (52,000 rpm) in order to decrease disturbances[6]. The observations were carried out preferably by the method of overlapped scales[5,7]; but in another series the optical method of an inclined slit, Svensson's method[8], which gives the image of the gradient of the refractive index directly, was used.

Since as the basis of the following calculation a Gaussian distribution was used[1], the sedimentation constant s_m which corresponds to the maximum of the sedimentation diagram or mode value was determined. The calculation was performed using the accepted equation:

$$s_m = \frac{1}{\omega^2} \frac{d \ln \chi_m}{dt} \quad \text{or of} \quad s_m = \frac{1}{\omega^2} \frac{\ln(\chi_2)_m - \ln(\chi_1)_m}{t_2 - t_1} \tag{1}$$

where ω is the angular rotor velocity of the ultracentrifuge, χ_m the distance between the maximum of the sedimentation diagram and the axis of rotation, and $(\chi_1)_m$ and $(\chi_2)_m$ are the positions of the maximum at the times t_1 and t_2.

In the first case the graph $\log \chi_m = f(t)$ was plotted and the mean value of $d \ln \chi_m/dt$ for the time of the experiment was established. This method of calculation is the best one if the temperature during the experiment does not change more than one to two degrees. If the temperature changes are greater, it is advisable to use the second formula and to take into account the correction for the viscosity change of the solvent during each pair of experiments.

The series of values of s_m thus obtained should then be averaged. Since the sedimentation constant is referred to the standard temperature of 20° C, it is necessary also to take into account the changes of density and partial specific volume. Finally, the value of s_{20} is given by the known formula[5]:

$$s_{20} = s_{t°} \frac{\eta_{t°}}{\eta_{20}} \frac{1 - V_{20}\rho_{20}}{1 - V_{t°}\rho_{t°}} \tag{2}$$

where η_{20} and $\eta_{t°}$, ρ_{20} and $\rho_{t°}$ and V_{20} and $V_{t°}$ are, respectively, the viscosity of the solvent, density of the solvent, and partial specific volume of polymer in the temperature range 20° C and t_1.

If, for the calculations Equation (1) is used, the correction term $\eta_{t°}/\eta_{20}$ is averaged for the whole temperature range; the second correction term is averaged for the whole time of the experiment, independent of the method of calculation. This is usually small.

The partial specific volume was determined in the standard way[5]. It is essential to make clear to which concentration c the experimentally measured value s_m should be referred.

It is clear that in the range of the sedimentation curve the concentration changes from 0 to the initial concentration c_0, and the experiments show that the sedimentation diagrams remain quite symmetric during the entire period of centrifugation. This means that the speed of motion of the diagram's maximum equals exactly the speed of sedimentation of the polymer near the bottom of the cell, where the concentration remains at all times equal to c_0. Strictly speaking, this is not quite correct, since, due to the sectorial shape of the cell, so-called centrifugal dilution takes place[5] and this leads to a decrease of c_0 during the experiment. This should result in a slight increase of s_m. However, as previously shown[9], in a given case this effect is compensated by the hydrostatic compression of the solution, which leads to an increase of the viscosity towards the bottom of the cell and to a decrease of the sedimentation constant approximately equal to the increase due to dilution. Both of these effects are insignificant. Therefore, the values of the sedimentation constant were related to the initial concentration but not to the mean concentration.

The coefficient of diffusion, D, was determined with the aid of Lamma's

diffusion apparatus, which was modified in our laboratory[10]. Temperature was controlled to $\pm 0.005°$ C, and photographs of the scale were automatically made every six hours. Calculation of D by the method of second and zero moments gives the mean weight coefficient of diffusion[6]:

$$D_w = D_{2m} = \frac{\int D dc}{\int dc}; \quad D_{2m} = \frac{d_{2m}^2}{2t} \tag{3}$$

where d_{2m}^2 is the square of a standard deviation of the diffusion diagram which is equal to the second moment divided by the zero moment.

In calculating by the method of ordinate and area, one obtains the coefficient of diffusion[6]:

$$D_A = \frac{\int dc}{\int D^{-1} dc}; \quad D_A = \frac{d_A^2}{2t} \tag{4}$$

where the standard deviation is calculated by the equation:

$$d_A = \frac{m_0}{\sqrt{2\pi} H} \tag{5}$$

in which m_0 is the area (zero moment) of the diagram of diffusion and H is its maximal ordinate.

If the fraction under investigation is sufficiently homogeneous, the values of the constants D_{2m} and D_A are within 5–7 per cent of each other.

Such agreement was found in our experiments in most cases. In cases where experiments show these values to be divergent, we preferred to use the value of D_A because the value D_{2m} is extremely sensitive to various low molecular-weight impurities which diffuse rapidly. Such impurities result in distortion of the diffusion curve, which then becomes non-Gaussian with development of "wings". Their height is small, but they increase appreciably the second moment of the figure and create a false impression of rapid diffusion. In contrast to this, the value of D_A is but slightly sensitive to the presence of low molecular-weight impurities.

The difference between D_A and D_{2m} due to such impurities is especially evident toward the beginning of an experiment. In the course of diffusion the coefficients approach each other. This also confirms the fact that the distortion is caused by rapidly diffusing low-molecular weight impurities.

Light scattering measurements using a nephelometer are described in detail elsewhere[11]. The accuracy of measurements made with the aid of this apparatus was 5 per cent. The principal aim of these measurements was to obtain the value of the second virial coefficient of the osmotic equation for correction of Svedberg's equation, which gives the apparent molecular weight[1]:

$$M_c = \frac{s}{D} \frac{RT}{1 - V\rho} \tag{6}$$

In this equation s and D are coefficients of sedimentation and diffusion obtained at the same initial concentration; V is the partial specific volume of the polymer; ρ is the density of the solvent; R is the gas constant; and T is the absolute temperature. As was shown in a previous paper[1], the apparent weight

TABLE II

Polymer	No. of fraction	$a_m \cdot 10^{13}$	$D_{3m} \cdot 10^7$	$D_A \cdot 10^7$	$M_c \cdot 10^{-3}$	$M_m \cdot 10^{-3}$
	1a*	5.86				
	1b	4.88	1.29	1.31	371	2182
	2	4.74			287	804
	3	4.47	2.04	1.05	215	425
K-1	4	4.40			200	362
	5	4.30	2.35	2.36	181	304
	6	4.00	2.63	2.71	148	208
	7	3.57	3.33	3.28	107	141
	8	2.75			39.5	41
K-2	1	1.730		1.90	138	425
(Fractions	2	1.708	2.34	1.98	126	329
1–5 in	3	1.529		2.40	96.5	183
cyclo-	4	1.484	2.60	2.45	81.5	136
hexane)	5	1.360	3.92	3.63	54.6	75
(Fractions	6	1.064	2.55	2.30	56.5	75
6–9 in	7	0.964	3.32	3.08	38.2	46
cyclo-	8	0.894	3.45	3.56	30.7	36
hexane)	9	0.748	7.05	6.87	13.4	14.3
	1	6.58	1.18	1.01	600	1080
	2	6.43			540	900
	3	6.07	1.47	1.43	419	610
	4	5.81	1.58	1.56	365	500
	5	5.59	1.78	1.77	309	402
	6	5.53	2.07	1.80	303	399
K-3	7	5.26			235	285
	8	5.16	2.26	2.31	224	268
	9	5.08			215	257
	10	5.00	2.33	2.37	208	246
	11	4.89	2.90	2.79	170	194
	12	3.30	10.6		31	32

* This fraction in the process of sedimentation showed the presence of an additional component representing 10 per cent by weight of the principal fraction. The additional component is denoted 1a.

is related to the true one by the expression $M_c = M/(1 + 2 BM_c)$. Thus it is necessary to know the second virial coefficient in order to go from the apparent weight to the true one using the equation:

$$M = \frac{M_c}{1 - 2BcM_c} \tag{7}$$

This is why the correction term for asymmetry of scattering was not taken into account in the light-scattering experiments[12]. It would give a more precise value of the molecular weight in the range of 10 per cent for the heaviest fractions, but could not appreciably influence the value of the coefficient B which is found from Debye's equation[13]:

$$\frac{Hc}{\tau} = \frac{1}{M} + 2Bc + \cdots \tag{8}$$

where H is the Debye optical constant; c the concentration in g./cc., and τ the turbidity of the polymer solution.

Practically, the value of $2B$, which is necessary for substitution in Equation (7) is found by plotting a graph according to the equation:

$$2B = \frac{\Delta \left(\dfrac{Hc}{\tau} \right)}{\Delta c} \qquad (9)$$

It is desirable to make the determination of $2B$ in the linear region at a small c value, where the higher virial coefficients do not exert much influence.

RESULTS. MOLECULAR WEIGHTS OF FRACTIONS

Table II gives the values of s_m, D and M_c. The apparent weight was calculated with the aid of Equation (6). The partial specific volume of K-1 and K-3 appears to be 1.075 cc./g. and of K-2 1.03 cc./g.

Since the values of D were not determined for all fractions, the interpolation graphs for $\log s_m = F_1(\log M_c)$ and $\log D = F_2(\log M_c)$ were plotted. The plots were found to be straight lines, and with their aid the values of M_c and D were found without difficulty.

These graphs are shown in Figure 1.

Using these graphs, the values D and M_c were found. In the interpolation process reproduced in Figure 1b, the strokes 2, 7, and 9 on the line D correspond
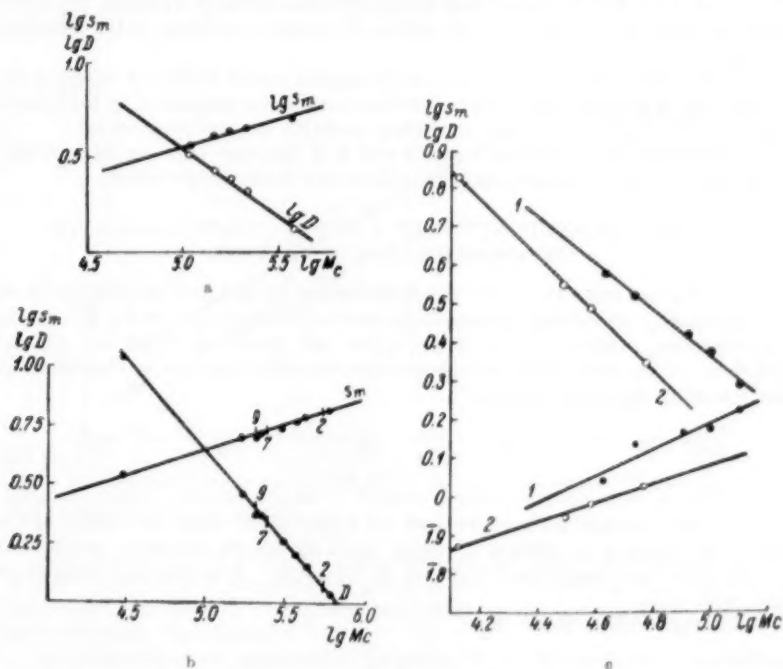
FIG. 1.—Relationship of s_m and D to the "apparent weight" M_c. Part a for K-1; c for K-2 (*1*—experimental data for cyclohexene, *2*—for cyclohexane); Part b for K-3.

to the values of the diffusion coefficients of fractions 2, 7, and 9. The value of M_c is automatically determined by the position of the strokes (corresponding to the measured values of s_m for these fractions) on the line s_m.

For K-1 rubber, the light scattering of fractions 1, 2, 4, and 6 was measured. In all cases $2B = 1.12 \times 10^{-3}$ cc./g.

The corresponding figure was given in the first paper[14]. For K-2 rubber, the light-scattering measurements were made on the nonfractionated sample. In cyclohexene $2B = 2 \times 10^{-3}$, and in cyclohexane 1.8×10^{-3} cc./g. Analogous measurement for K-3 gave $2B = 0.37 \times 10^{-3}$ cc./g.

In the last column of Table II the true molecular weights are given, which were calculated from Equation (7). Since the calculation was made by means of the mode value of the sedimentation constant s_m, the resultant molecular weight is also the mode weight; i.e., the most probable weight of the weight distribution

$$\frac{dw}{dM} = q_w(M)$$

and is denoted by M_m. As indicated in the previous paper, in the case of narrow symmetric fractions the mode weight coincides with the average weight M_w.

In Figure 2 the log s_m is plotted versus the logarithm of various mean weights (according to the data of Tables I and II).

Direct comparison of the values of M_m with various mean values of M from Table I or from Figure 1 show that in the principal series of fractions, the molecular weights M_n, M_η, M_m coincide within the range of accuracy of the measurements.

In contrast to this, the extreme fractions give rather scattered values of M. In the case of the low molecular-weight fractions this is stipulated by their large polydispersion and by the fact that they probably are not symmetric.

Concerning K-1 Fractions 1 and 2 and K-2 Fraction 1, it can be said that there may be other possible reasons. These we shall discuss below.

RELATIONSHIP BETWEEN s AND M. DEPENDENCE OF s ON THE CONCENTRATION

The effect of concentration[15] was investigated for K-1 and partially for K-3.

In Figure 3 the results of measurements for fractions 3, 5, and 7 K-1 in the concentration range of 0 to 4×10^{-3} g./cc. are given. As is known, the dependence of the sedimentation constant on concentration can be expressed by the following empirical equation[6]:

$$s = \frac{s_0}{1 + k_s c} \tag{10}$$

To make extrapolation convenient for a number of cases, the values of $1/s$ and $1/s\eta_r$ where η_r = relative viscosity, were plotted on the same graph. At $c = 0$, both lines should come together at one point. This precisely determines the value of s_0.

It is curious that in all cases:

$$\frac{1}{s} = \frac{1}{s_0} + k''c \tag{11}$$

i.e., k_s in Equation (10) equals $k''s_0$. If s is expressed in "Svedbergs" (10^{-13} CGS) and c in g./cc., $k'' = 40$. Hence for these rubbers the following relationship

$$s = \frac{s_0}{1 + k''s_0 c} \tag{12}$$

enables us to find s_0 by using the value of s measured at a finite concentration for any fraction.
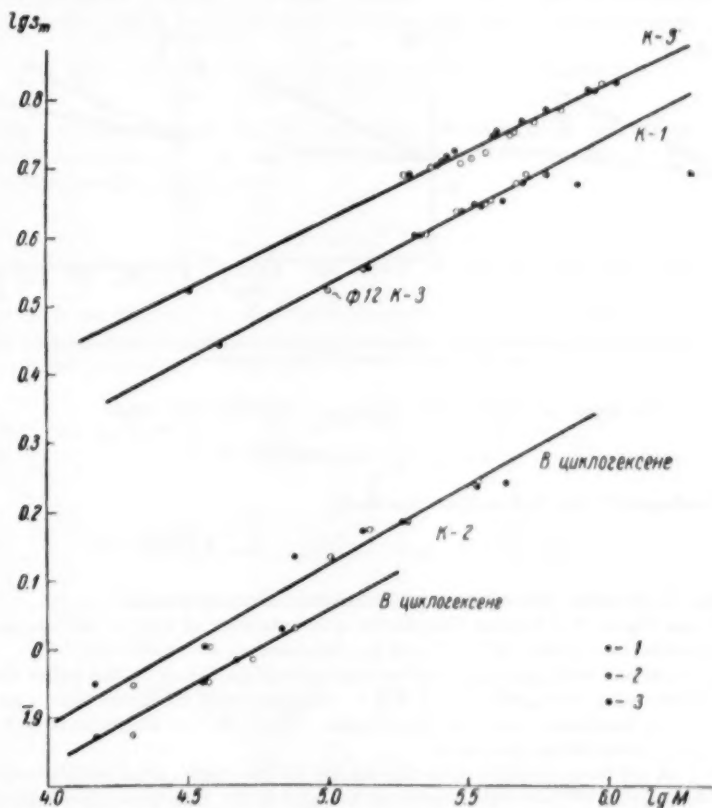
Fig. 2.—Dependence of s_m on the "true weight" M_m and other mean weights. Using this graph, the parameters A and α', which are necessary for transition to the distribution dw/dM, can be determined. Point 1—M_n, M; Point 2—M_w; Point 3—M_m.

The dependence of s_0 on M is expressed by the Debye-Bueche relation: $s_0 = A M^{1-\alpha}$, where α is the so-called penetration parameter (its value is 1 for a molecular conglomerate completely penetrated by the solvent and 0.5 for one not completely penetrated[17]).

In order to find the penetration parameter α, one needs to plot the graph of $\log s_0 = F(\log M)$. In Figure 4a $\log M$ is plotted on the abscissa and $\log s_0$ and $\log s(c)$ on the ordinate for K-1.

It is curious to note that the value of $s(c)$ (measured at the finite concentration $c = 2 \times 10^{-3}$) is related to the molecular weight by the equivalent relation: $s = A, M^{1-\alpha'}$. Here $\alpha' > \alpha$ and in this case is no longer a penetration parameter. This relation follows also from the data illustrated in Figure 2.

This can all be explained by the fact that at small concentrations the denominator in Equations (10) and (12) is so little dependent on molecular weight that it can be written as $1 + k''s_0 c = \phi(M) = KM^\beta$. The points for $\log \phi(M)$ in Figure 4a show that this is actually so.
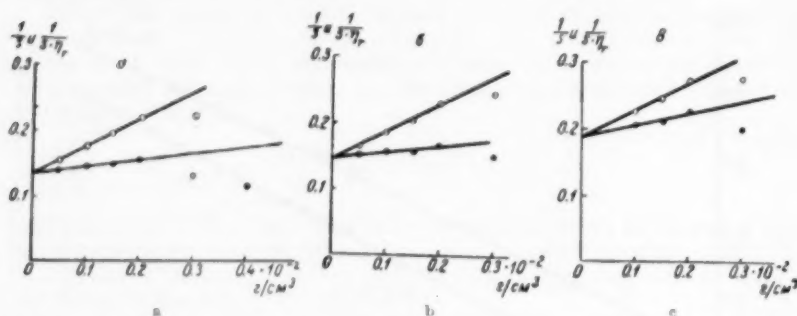
FIG. 3.—Dependence of the sedimentation constant on the concentration for some fractions of K-1. Part a fraction 3; Part b fraction 5; Part c fraction 7.

From the figure we find for K-1 that $s_0 = 0.159M^{1-0.705}$, while

$$[s(c)]_{c=2 \cdot 10^{-3}} = 0.282M^{1-0.762} \tag{13}$$

Analogously, for K-3 rubber, one finds:

$$s_0 = 0.061M^{1-0.67} \quad \text{and} \quad [s(c)]_{c=2 \cdot 10^{-3}} = 0.372M^{1-0.791} \tag{14}$$

For K-2 rubber, the effect of concentration was not studied.

From Figure 1 it follows that at the concentration of 2.45×10^{-3} g./cc. in cyclohexene, $s = 0.0861M^{1-0.764}$ and in cyclohexane, $s = 0.0804M^{1-0.77}$.

Comparison with previous rubbers led us to think that here the value of α is also of the order of magnitude of 0.6–0.7 Consequently all three rubbers are in solution as semipenetrated conglomerates. Here K-1 is characterized by a very large penetration parameter.

Let us try now to make clear the reason for too high values of M_m according to Equation (7) for heavy fractions K-1 and K-2. The reason probably lies in the fact that diffusion and sedimentation are not measured at identical concentrations. We have already mentioned that the sedimentation constant, measured experimentally, should be related to the polymer concentration c_0. The corresponding thermodynamic correction term should be taken equal to $1-2BM_c c_0$, but diffusion is actually measured in the range of c_0 to 0. As was shown by Gralen[16], Jullander[6], and Schulz[18], the measured diffusion coefficient should be related to the mean concentration, i.e., approximately to $c_0/2$.

Thus, on substituting in Svedberg's Equation (6) the value of D which is actually related to the concentration $c_0/2$, we slightly diminish the value of $1-2M_c B_c$ and obtain exaggerated molecular weights. This will be the more

pronounced, the higher the molecular weight and the larger is the virial coefficient B.

For example, for K-3 the virial coefficient is small and therefore even for the first fraction ($M = 10^6$) Equation (7) gave the correct result. In contrast to this, the first fraction of K-2 has a lower molecular weight ($M = 350,000$), but a large value of $2B$, so again, the recompensation takes place. For the principal series of fractions the relation of the values M and $2B$ is such that lowering the diffusion coefficient has practically no influence on the final result. Since for all fractions we have on hand independently reliable values for the molecular weight, the condition indicated does not in general play an essential role.

MEASUREMENT OF DEGREE OF POLYDISPERSION OF THE FRACTIONS

The polydispersion of the fractions was determined by the method of Gaussian distribution[20]. As was shown by us, in one fraction the distribution can be expressed by the equation:

$$\frac{dw}{dM} = q_w(M) = \frac{w}{\sqrt{2\pi}\,\mu} e^{-(\Delta M)^2/2\mu^2} \tag{15}$$

(where w is the weight of the fraction and μ is the standard deviation); then the distribution of sedimentation constants and of displacements ξ also is expressed by Gaussian functions:

$$q_w(s) = \frac{dw}{ds} = \frac{w}{\sqrt{2\pi}\,\sigma} e^{-(\Delta s)^2/2\sigma^2}; \quad \sigma = \mu(1 - \alpha)\frac{s_m}{M_m} \tag{15a}$$

and

$$q_w(\xi_s) = \frac{dw}{d\xi} = \frac{w}{\sqrt{2\pi}\,\delta} e^{\xi^2/2\delta^2}; \quad \delta = \omega^2 \chi_m t\sigma \tag{15b}$$

If $q_w(\xi)$ includes displacement due to diffusion, then for a Gaussian fraction, we have again:

$$q_w(\xi_s, \xi_D) = \frac{w}{\sqrt{2\pi}\,\overline{\xi^2}} e^{-t^2/2\overline{\xi^2}}; \quad \overline{\xi^2} = 2D_w t + \overline{\delta}^2 \tag{15c}$$

The standard deviation $\sqrt{\overline{\xi^2}}$ of the sedimentation diagrams was calculated by the method of ordinate and area, since in this case the sedimentation diagram is automatically substituted by the equivalent Gaussian distribution. It is useful here to reproduce the equivalent distribution and to compare it with the real diagram.

In Figure 5 of the first paper[1], three typical diagrams were given. Experimentally there were no remarkable deviations from the Gaussian form for most of the fractions investigated. Thus, if F is the area of the sedimentation diagram, and H is the maximal ordinate, then:

$$\xi^2 = \frac{F^2}{(\sqrt{2\pi}\,H^2)} K^2 \tag{16}$$

where K is the photographic correcting multiplier[5]. From this one finds:

$$\bar{\delta}^2 = \frac{F^2}{2\pi H^2} K^2 - 2\beta D_w t \tag{17}$$

where β is the temperature coefficient which brings D_w to the mean temperature of the experiment. Obviously it is possible to use a graphic method, whereby plotting:

$$F(\chi_m{}^2 t) = \frac{\bar{\xi}^2}{2t} = \beta D_w + \frac{\bar{\delta}^2}{2t} = \beta D_w + \frac{w^2 \sigma^2}{2} \chi_m{}^2 t \tag{18}$$

makes possible separate displacements due to sedimentation and diffusion, even if D_w is not entirely independent.
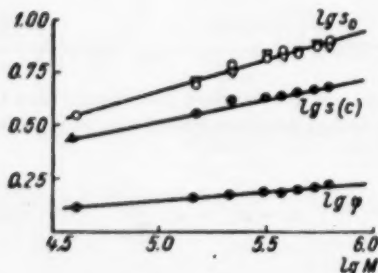
FIG. 4a.—Another method of investigation of dependence on concentration. The value $1 + k''$ sc at $c = 2 \times 10^{-3}$ g./cm.[3] as a weak function of molecular weight ϕ (M) can be written in an equivalent form constant M^β, or $\log \phi = $ constant $+ \beta \log M$. Summation of $\log \phi$ and $\log s(c)$ values corresponding to a given concentration should give the value of $\log s_0$. These values are denoted by triangles, and coincide well with values $\log s_0$ (circles) obtained direct from the graph of the type in Figure 3.
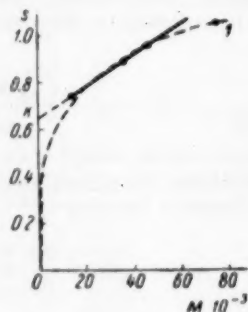
FIG. 4b.—Deviation from the Debye-Bueche relationship at small molecular weight values. 1—Theoretical curve $s = 0.0804\ M^{0.5}$.

The coincidence of $(\bar{\xi}^2/2t)_{t=0}$ with the value βD_w measured separately is a supplementary sign that a fraction is Gaussian. For the determination of the quality of a fraction it may be satisfactory to confine ourselves to a comparison of σ and s_m for each fraction or to the determination of the dispersion coefficient:

$$\Delta = \frac{\mu}{M_m} = \frac{1}{1 - \alpha} \frac{\sigma}{s_m} \tag{19}$$

The dispersion coefficient is a characteristic parameter which enables one to determine to what extent it is valid to describe the distribution $q_w(M)$ by the Gaussian function.

Indeed, it is known that the ordinates of Gaussian curves are practically zero in the limits of three standard deviations. Therefore, strictly speaking the dispersion coefficient cannot exceed 0.33.

If this coefficient, which is computed from experimental values of σ, s_m and M_m, is larger than 0.33 the distribution cannot be strictly Gaussian, since it would overlap the domain of negative values of M.

It is useful to recall here the theoretical considerations which were published in the first paper. Equation (15b) describes exactly the relationship between distributions $q_w(\xi)$ and $q_w(s)$. In contrast to this, Equation (15a) on strict analysis shows that it is only approximate. We emphasized that the Gaussian distribution $q_w(s)$ and $q_w(M)$ can be counted simultaneously only in the case when $\mu/M \leqq 0.25$. In reality, if the distribution of the sedimentation constants $q_w(s)$, obtained from experiment, may well approximate the Gaussian curve, then the distribution of molecular weights will be described by the equation:

$$q_w(M) = \frac{dw}{dM} = \frac{dw}{ds}\frac{ds}{dM} = q_w(s)(1-\alpha)\frac{s}{M} \tag{20}$$

If then

$$q_w(s) = \frac{w}{\sqrt{2\pi}\sigma} e^{-(\Delta_s)^2/2\sigma^2}$$

then

$$q_w(M) = \frac{w}{\sqrt{2\pi}}\frac{1-\alpha}{\sigma}\frac{s}{M} e^{-(\Delta M)^2/2\mu^2} \tag{21}$$

where

$$\mu = \frac{\sigma}{1-\alpha}\frac{M_m}{s_m}$$

We stress here the fact that in deducing the principal relations[1] we proceeded in the opposite direction: From distribution $q_w(M)$ we went to $q_w(s)$ etc.

In the range of molecular weights over 100,000 and at small values of $\Delta = \mu/M_m$ it is possible to neglect the pre-exponential multiplier, ds/dM, or s/M and assume the distribution $q_w(M)$ to be Gaussian.

At $\mu/M_m > 0.25$ the distribution may turn out to be asymmetric. Practically, however, if $\mu/M_m \leqq 0.33$, one may neglect this fact and instead of calculating by means of Equations (20) or (21) merely plot the equivalent Gaussian distribution, using experimental values of w, μ and M_m with the coordinates M and dw/dM. By summation of distribution $q_w(M)$ for each fraction, the total distribution may be easily found by:

$$Q_w(M) = \sum_{i=1}^{n} q_w(M)_i \tag{22}$$

Thus the distributions for the K-1 and K-3 rubbers can be plotted. However, as we shall see in the next section, the K-2 rubber has extremely broad fractions, and such a calculation cannot be correct. It will lead to the displacement of part of the distribution to the range of negative molecular weights.

Experiments showed that the curves $q_w(\xi)$ for this rubber, found with the aid of the ultracentifuge, approximate very well Gaussian functions.

This enabled us to make the calculation for K-2 rubber in practically the same way as for K-1 and K-3. After excluding diffusion, the equivalent Gaussian distribution was plotted for each fraction, using the sedimentation constants $q_w(s)$. All of these distributions were then summarized for all the frac-

tions, taking into account the relative weights of each fraction. In this way the summary distribution $Q_w(s) = \sum q_w(s)_i$, which transforms into the summary distribution of M according to Equation (21), was obtained.

For K-1 and K-3 rubbers, both methods of calculation give identical results, as is understandable; however, the second method is more convenient practically.

For K-2 rubber, which has broad fractions, calculation by the second method takes into account automatically the fact that since the fractions are Gaussian to a sufficient degree of accuracy in sedimentation constants $(\sigma/s_m \leqslant 0.25)$, they cannot be Gaussian in molecular weights $(\mu/M_m \geqslant 0.5)$.

However, the result obtained here is somewhat unexpected (thin line in Figure 10). As the ordinates approach zero M, they show a tendency to increase continuously, which evidently does not correspond to the real picture.

For the fractions with the lowest molecular weight (with molecular weights $< 50,000$) a calculation using Equation (21) is impracticable. The relation of s/M in this equation approaches infinity as M approaches zero.

Thus one low fraction which is a relatively small percentage of the polymer weight can cause significant distortion of the distribution curve in the range of low molecular weights, if the μ/M_m for them is not too small (this is shown by the dotted line in Figure 9, where distortion is caused by the last fraction).

This seeming mathematical difficulty has evident physical significance. The derivative, ds/dM, which tends toward infinity on lowering of the molecular weight, gives evidence that the resolution power of the ultracentrifuge increases infinitely for low molecular-weight products. It is clear that this is wrong.

The error is caused by the fact that the Debye-Bueche function $s = AM^{1-\alpha}$ cannot be correct at low molecular weights of polymers. This function is correct for macromolecules, which can be called agglomerates more or less penetrated by the solvent. If the degree of polymerization is of the order of magnitude of tens, the polymer cannot be counted as an agglomerate. It will be a streamlined thread.

With decrease of the degree of polymerization, it will tend to the configuration of an ideally streamlined rod. Thus, when the molecular weight decreases (remaining, however, essentially larger than that of the monomer) s approaches a constant value K, which is independent of the molecular weight. This is obvious from Svedberg's formula: $s = [M(1 - V\rho)/f]$; when the rod is perfectly streamlined: $f = \chi M$, and M in the numerator and denominator cancel out.

At low molecular weights the correct relationship of $s = s(M)$ can be developed into a series and should lead to the expression in a first approximation of:

$$s = K + K'M \qquad\qquad (23)$$

Such a view of the function, $s = s(M)$, follows from the physical structure of short molecules of a polymer; Figure 4a illustrates the relationship, $s = s(M)$, near zero for the K-2 rubber.

The Debye-Bueche function cannot be developed into a series at small M values because the first derivative ds/dM is infinite. This last fact contradicts experimental data and all that is known about the structure of polymers. Therefore, there is no doubt that for the fractions with the smallest molecular weights, the transition from s to M must be made with the aid of Equation (23). As before, $q_w(M) = q_w(s)(ds/dM)$, but now ds/dM is not equal to $(1 - \alpha)(s/M)$, but simply to the constant K'.

Thus, for the fractions with $M < 5000$ and having a large coefficient of dispersion:

$$q_w(M) = \frac{dw}{dM} = q_w(s)\frac{ds}{dM} = K'q_w(s) \qquad (24)$$

This eliminates completely the anomaly at low molecular weights discussed above.

Practically, the calculation is performed in the following way. On the co-ordinates s and dc/ds the Gaussian curves which represent each separated fraction are plotted. Each curve represents the distribution of s_m for a given fraction. The maximal ordinate is found from the condition of the proportionality of the area, limited[19] by the curve dc/ds, to the weight part of a fraction w_i, that is:

$$H = \frac{w_i}{\sqrt{2\pi}\,\sigma_i} \qquad (25)$$

Then, the summation of the fractions and transition to distribution $q_w(M)$ using Equation (21), i.e., $q_m(M) = (1 - \alpha)(s/M)q_w(s)$, is made. If the distribution contains low molecular fractions, parts of which cannot be neglected, the summation of the curves, dc/ds, should be made for all fractions excepting the low molecular-weight ones.

For the other fractions recalculation from $q_w(s)$ to $q_w(M)$ is made, using Equation (23) for each fraction separately, and the results are summarized with the result of recalculation for the principal series of fractions.

QUALITY OF FRACTIONS

A. SHAPE OF FRACTIONS

In the previous section we showed one confirmation for the hypothesis concerning the Gaussian character of the function, $q_w(M)$, which was manifest in the fact that the various mean molecular weights coincided satisfactorily.

As was shown in the previous paper, the sedimentation diagrams do not differ practically from Gaussian curves. In Figure 6 of the previous paper[1] the graph $\overline{\xi^2}/2t = F(\chi_m^2 t)$ was reproduced. By means of it the values of σ and βD_w for the K-2 fractions 1–5 were calculated.

Table III gives the values of $(\overline{\xi^2}/2t)_0$ obtained in a similar way for most of the fractions and for comparison the values of βD_w from independent experiments. As is evident, in all cases, the coincidence is very good with but one exception. Thus, the distribution, $q_w(s)$, for most of the fractions should be of Gaussian character.

B. BREADTH OF FRACTIONS

Let us note first of all that we dealt with sufficiently narrow fractions, since the parameters s_m and D never overlapped. It is expedient to evaluate the broadness of fractions with respect to $\Delta = \mu/M_m$, as well as by the absolute value of μ.

In Table IV the experimental values of s_m, σ and M_m for all three rubbers are given and also the calculated values of μ/M_m and μ.

The standard deviation was calculated by the equation:

$$\mu = \frac{\sigma}{1-\alpha}\frac{M_m}{s_m}$$

TABLE III

Polymer	No. of fraction	$(\bar{p}/2t)_{t=0} \cdot 10^7$	$\beta D_w \cdot 10^7$
	2	1.75	1.74
	3	2.10	2.16
K-1	4	2.20	2.20
	5	2.20	2.49
	7	3.50	3.51
	8	7.00	6.90
	1	2.80	2.10
	2	2.00	2.20
K-2	3	2.45	2.54
	4	2.60	2.75
	5	3.70	3.90
	2	1.20	1.16
	4	1.73	1.65
	5	1.85	1.87
	7	2.25	2.32
K-3	8	2.35	2.46
	9	2.55	2.52
	10	2.66	2.54
	11	3.35	3.07
	12	11.1	10.8

TABLE IV

Polymer	No. of fraction	$\delta_m \cdot 10^{14}$	$M_m \cdot 10^{-2}$	$\sigma \cdot 10^{13}$	σ/s, %	$\Delta = \mu/M$, %	$\mu \cdot 10^{-2}$
	1	4.88	600	0.26	6.35	29.3	175
	2	4.74	525	0.194	4.10	18.9	99
	3	4.47	425	0.168	3.76	17.4	74
K-1	4	4.40	362	0.130	2.96	13.6	49
α' 0.783	5	4.30	304	0.262	6.10	28.2	93
	6	4.00	208	0.235	5.9	27.2	57
	7	3.57	146	0.263	7.35	34.0	50
	8	2.75	41	0.766	27.8	128	53
	1	1.730	350	0.400	23	—	—
	2	1.708	329	0.269	15.7	—	—
	3	1.529	183	0.168	11	—	—
K-2	4	1.484	136	0.161	10.8	—	—
α' 0.77	5	1.360	100	0.159	11.7	—	—
	6	1.064	75	0.160	15	—	—
	7	0.964	46	0.190	19.7	—	—
	8	0.894	36	0.206	23	—	—
	9	0.748	14.3	0.200	26.7	—	—
	1	6.58	1080	0.35	5.32	25.4	271
	2	6.43	900	0.304	4.8	23	207
	3	6.07	610	0.219	3.6	17.2	105
	4	5.81	500	0.233	4.0	19.2	96
	5	5.59	402	0.218	3.9	18.7	75
K-3	6	5.53	399	0.240	4.34	20.8	83
α' 0.791	7	5.26	285	0.215	4.1	19.6	56
	8	5.16	268	0.198	3.83	18.3	49
	9	5.08	257	0.227	4.46	21.4	55
	10	5.00	246	0.249	4.98	23.9	59
	11	4.89	194	0.434	8.88	42.5	82
	12	3.30	32	0.620	18.8	111	36

The values of α' which are necessary for calculation are also given in Table IV.

Let us now consider in summary the quality of the fractions.   It is evident that almost all the K-1 and K-3 fractions (except the last ones) have small dispersion coefficients which warrant their being regarded as strictly Gaussian.

In contrast to this, for all the fractions of K-2 the value of Δ is much greater than 40 per cent, and therefore for this rubber it is not permissible to make any further calculation by summation of the Gaussian functions of molecular weights.   However, with the aid of the artifices indicated in the preceding section on the "Measurement of Degree of Polydispersion of the Fractions", it is possible to overcome this difficulty and to reproduce the function $q_w(M)$ on the basis of the equivalent Gaussian distributions $q_w(s)$.
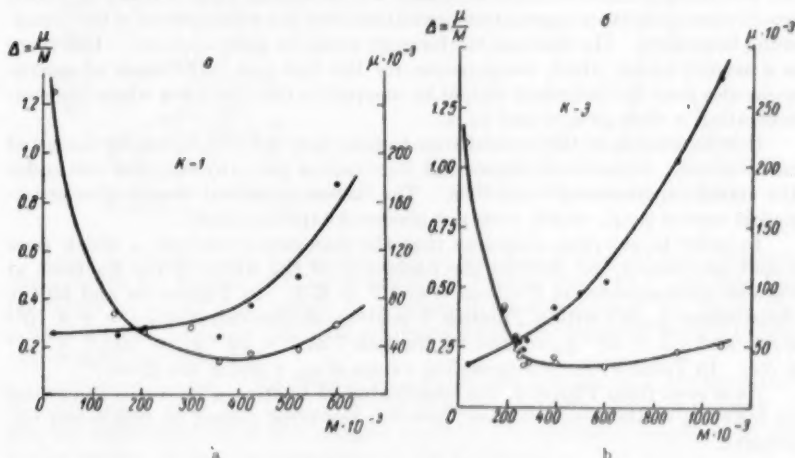
FIG. 5.—Dependence of standard deviation and dispersion coefficient on the molecular weight.   Part a for K-1 and Part b for K-3 (points for standard deviation, circles for dispersion coefficient).

Another essential conclusion which can be drawn from the table is the fact that on transition from the higher fractions to the lower the relation μ/M_m passes through a very diffuse minimum at the same time as the absolute half width of the distribution in general decreases (Figures 5a and 5b).   This corresponds exactly to the predictions of the theory of fractionation.   Analogous results were obtained by Rånby[20] in an investigation of nitrocellulose.

It seems to be true that the degree of fractionation for K-2 is poorer than for the other two rubbers.

Finally, it should be noted that the values found by us for μ are correct, i.e., they are independent of the concentration at which the measurements are made. We illustrated in the first paper that by substituting the value of α', corresponding to the concentration, in the relation: $\mu = (\sigma/1 - \sigma)(M_m/s_m)$, we introduced a correction for concentration.

However, there is an additional source of error which is not taken into account by this correction.   Since the sedimentation of macromolecules near the boundary takes place at variable concentration of polymer,

$$c = \int_{x0}^{x} \frac{dc}{d\chi} \, d\chi,$$

TABLE V

No. of fraction	$c \times 10^3$	s_∞	σ	σ'
5	2	4.30	0.262	0.783
	1.5	4.97	0.385	0.762
7	2	3.57	0.263	0.783
	1	4.44	0.526	0.744

the molecules which are moving slower (lighter molecules) are found in the region where the concentration is closer to zero; the macromolecules which are moving faster (heavier molecules) are found in the region where the concentration is always close to c_0. This leads to some contraction of the boundary, i.e., the broadening measured experimentally will be smaller than it really is, which would correspond to a constant concentration over the whole extent of the broadening boundary. (In this case the formula would be quite correct.) But there is a second factor which compensates for the first one. Diffusion of macromolecules near the boundary should be unequal in the directions where the concentration is close to zero and to c_0.

It is impossible at the present time to take care of these factors by means of calculations. Experiment shows that they cannot play any essential role under the actual experimental conditions. The factors indicated should give asymmetric curves $q_w(\xi)$, which were not observed experimentally.

In order to convince ourselves that the standard deviations μ which were found are correct, we checked the constancy of the width of the fractions at various concentration in fractions 5 and 7 of K-1. In Figures 6a and 6b the distribution $q_w(M)$ within Fraction 5 is given at concentrations $c = 2 \times 10^{-3}$ g./cc. and 1.5×10^{-3} g./cc. and for fraction 7 at 2×10^{-3} g./cc. and 1×10^{-3} g./cc. In Table V the corresponding values of s_m, σ and σ' are given.

As is seen from Figure 6, the broadening of fraction μ increases somewhat on lowering of the concentration; however the error caused by this is not significant.

THE DISTRIBUTION FUNCTION

For the sake of illustration, the procedure of summation of fractions and distribution, $Q_w(s)$, for K-1 is reproduced in Figure 7.
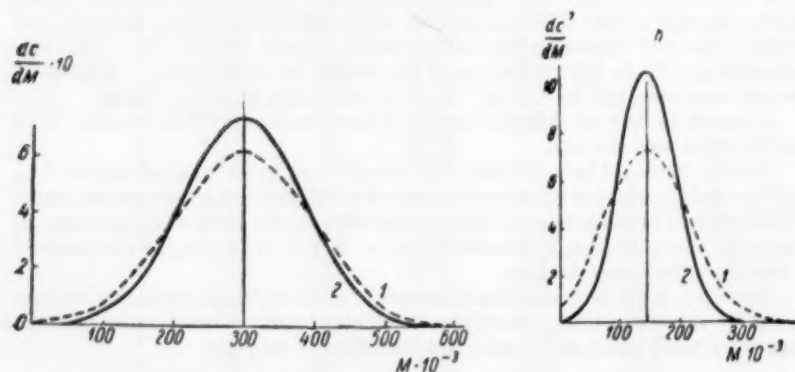
Fig. 6.—Calculated standard deviation as function of concentration. Left diagram for Fraction 5, K-1; for 1 $c = 1.5 \times 10^{-3}$, for 2 $c = 2 \times 10^{-3}$. Right diagram for Fraction 7, K-1; for 1 $c = 1 \times 10^{-3}$, for 2 $c = 2 \times 10^{-3}$.
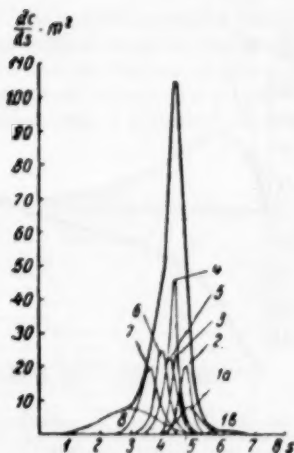
FIG. 7.—Summation of fractions and distribution $q_w(s)$ for K-1.
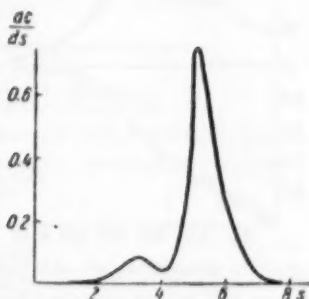
FIG. 8.—Distribution $q_w(s)$ for K-3.

In an analagous way the function $Q_w(s)$ for K-3 (Figure 8) was obtained. Final results for K-1 and K-2 are presented in Figures 9 and 10. The light line in Figure 10 shows what would be obtained by calculation of the whole distribution using Equation (21) without introducing the correction for low molecular-weight fractions 6–9.

In Figures 11 and 12 the distributions $q_w(M)$ for K-1 and K-2 are presented in comparison with the analogous distributions obtained by the method of graphic differentiation of the integral curve of precipitation, described in the earlier section on the "Fractionation of the Polymers".

As is evident, this method gives in general the correct picture, but imminently leads to the sharpening of the maximum and to the loss of some real details.
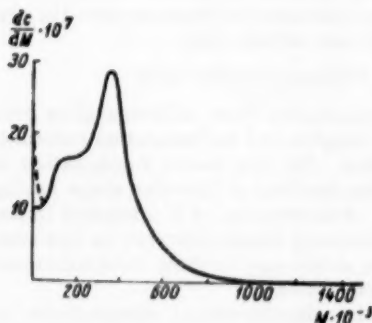
FIG. 9.—Distribution $q_w(M)$ for K-1. The distortion which originates if the peculiarity of the function $s(M)$ at small molecular weights is not taken into account is shown by the dotted line.
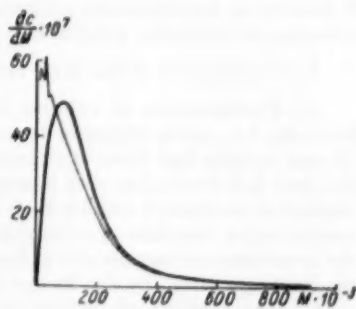
FIG. 10.—Distribution $q_w(M)$ for K-2. The thin line shows the distorted result obtained by calculation for the last four fractions using Equation (21) instead of Equation (24).
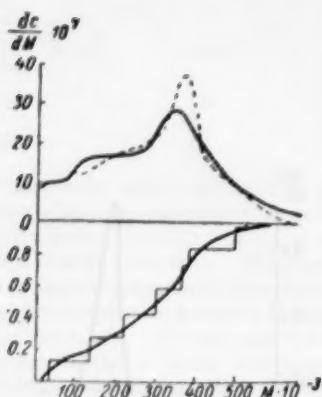
FIG. 11.—Comparison of distributions $q_w(M)$ obtained for K-1 by the method of ultracentrifuge (solid line) and by graphic differentiation of the steplike integral curve of precipitation (dotted curve).
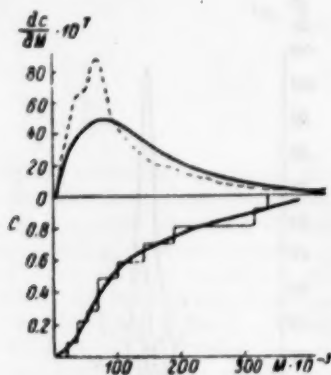
FIG. 12.—Comparison of distributions $q_w(M)$ obtained for K-2 by the method of ultracentrifuge (solid line) and by graphic differentiation of the steplike integral curve of precipitation (dotted curve).

SUMMARY

In an investigation of three different synthetic rubbers, methods of fractionation were examined and measurements were made of the molecular-weight distribution by analysis of fractions[1].

The following conclusions may be drawn.

(1) The method of equivalent Gaussian distributions correctly reproduces the distribution within each fraction and makes it possible to distinguish the broadening of the sedimentation curve attributable to diffusion and that attributable to polydispersion.

(2) The method of accounting for the final concentration of the solution under investigation introduced by us result in correct values of molecular weights of fractions and correct values of standard deviations.

(3) Comparison of a series (about 10) of fractions of a given polymer makes it possible to transpose the sedimentation constant distributions into the distribution of molecular weights in a simple and natural way.

An investigation of the three rubbers demonstrates two facts.

(1) Fractionation of rubbers by precipitation from solutions gives true fractions, i.e., mode values of molecular weights and sedimentation constants do not overlap but form continuous series. By this means fractionation of K-1 and K-3 resulted in very homogeneous fractions of Gaussian shape having dispersion coefficients smaller than 0.33. Fractionation of K-2 resulted in less homogeneous fractions of somewhat asymmetric shape; however, in this case, the broadness and asymmetry of fractions, as it is easy to show, does not exceed the limits predicted by the theory of fractionation.

(2) The method of determination of molecular-weight distributions by tracing the steplike curve of precipitation, with subsequent smoothing by graphic differentiation, gives a correct picture of the distribution function of polymers for molecular weights; however, the finer details of distribution can be distorted and lost in tracing the steplike curve.

The molecular-weight distributions of synthetic rubbers by the ultracentrifuge method must be closely related to the process of genesis of a polymer, i.e., with the mechanism of the polymerization reaction. Thus, with proper experimental technique our method can be applied to the investigation of various mechanisms of polymerization and polycondensation.

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EFFECT OF ELONGATION ON THE PROTON MAGNETIC RESONANCE OF NATURAL RUBBER *

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Several authors[1-4] have already reported their studies on natural rubber by the method of proton magnetic resonance. However, since there has been little work on the effect of elongation on proton magnetic resonance absorption, we present our investigation on the proton magnetic resonance absorption of stretched samples of vulcanized natural rubber.

For this experiment a large permanent magnet[5] shown in Figure 1 was constructed. The magnetic field strength was 6090 gauss at the center of the gap at 18° C. The magnet had a field inhomogeneity of about 0.01 gauss in a 0.2 cc. sample.

The derivatives of the resonance line were recorded at fixed frequency, changing the magnetic field linearly in time with an automatic electronic bias control[6].

Control of the temperature from liquid nitrogen to room temperature was performed by a cryostat similar to that described by Gutowsky[6].

. The sample was a commercial rubber ring (cross-section 1×1 mm.) which might have had a sulfur content of a few per cent and had good rubber elasticity. Before the experiments, the samples were annealed for a day or more at about 30° C in an electric oven. At first, the resonance of the sample was observed in the unstretched state. Then, the reannealed sample, was stretched to 500% elongation by winding it around a wood bar (1 mm ϕ) to its maximum, and the resonance absorption was observed.

Figure 2 is a plot of the resonance line width as a function of temperature for stretched and unstretched samples. Over the whole temperature range studied, the line shapes were simple and had no structure. The overall features of the two curves are comparable to those found in previous studies by others[1-3]. The line widths for the two samples were nearly equal from room temperature to about −15° C. Some differences first appeared below −20° C. The line width of the unstretched sample increased markedly at about −38° C and that of the stretched one increased at about −30° C. Below these temperatures, the broadening of the line width resulting from the decrease of segmental motion was observed in the regions from −38° C to −52° C for the unstretched sample and from −30° C to −45° C for the stretched one. Below this, second regions of broadening appeared due to decrease of rotational motion of CH_3 groups. Finally the line widths became constant below −80° C and −70° C with values of about 9.3 gauss and 10.5 gauss for the unstretched and stretched samples, respectively. The molecules would be rigid in this range.

These results indicate that elongation of rubber affects the proton magnetic resonance absorption both in line width and transition temperature. It might
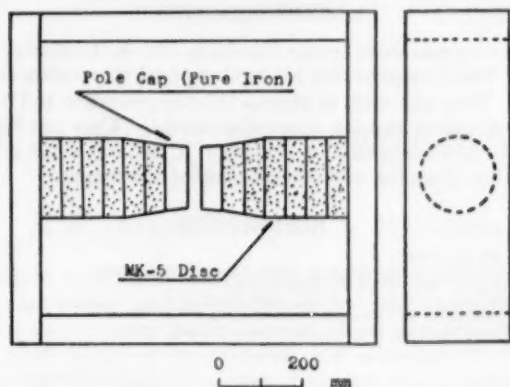
FIG. 1.—The permanent magnet.

be suggested that the orientation of molecules along the direction of elongation would hinder the segmental motion and cause the increase of line width mainly in this region.   The second moments in rigid state calculated from the experimental data were about 20.3 gauss^2 and 18.5 gauss^2 for the stretched and unstretched samples, respectively.   The value for the unstretched sample is consistent with previous results[3].   Therefore, the difference of 1.8 gauss^2 may be attributed to the increase of intermolecular second moment caused by molecular orientation.
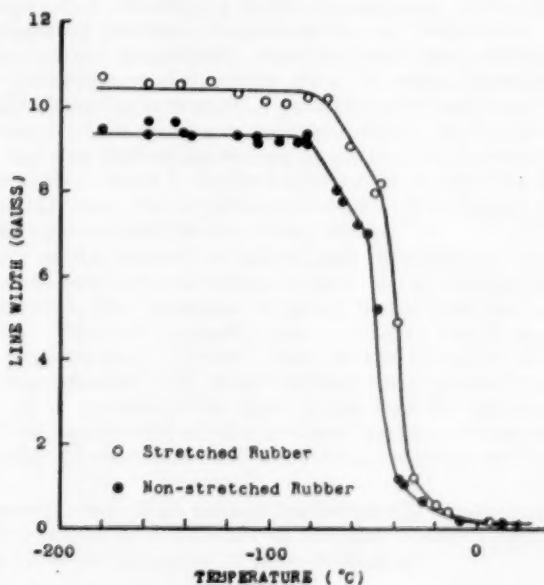
FIG. 2.—The proton magnetic resonance line width of stretched and unstretched rubber as a function of temperature.

ACKNOWLEDGMENT

The authors express their hearty thanks to Mr. K. Ishibashi, vice-president of Bridgestone Tire Company, for his kind support in constructing the permanent magnet.   They also wish to express their appreciation to Dr. A. Isihara for suggesting the problem and for many discussions.   They are further indebted to Professor N. Bloembergen and Professor H. Kumagai for kind advice and suggestions in our planning and construction of the magnet.

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THE NATURE OF SELF-ADHESION (TACK) OF POLYMERS. I *

S. S. Voyutskiĭ and Yu. L. Margolina

At the present time, ideas concerning cohesion, adhesion, and self-adhesion (self-sticking) are widely used for explaining the phenomena observed in gluing with polymeric substances. But the investigators, in developing the theory of gluing, pay most attention to cohesion and adhesion. Self-sticking (self-adhesion) has thus far remained unstudied and has no satisfactory explanation. Researches devoted to self-sticking are very few. Mention should be made here of the work of Zhukov and Talmud[1], who separated self-sticking from the total complex of adhesive properties, proposed the term autohesion, and were the first to study this property experimentally. Furthermore, we must mention the researches of Priklonskaya[2] and of Maslovskiĭ and Popova[3], who investigated the self-sticking of industrial materials (rubber mixtures). Finally, the question of self-sticking of polymeric substances was touched upon in a very small number of researches of foreign authors[4-6]. It should be noted however that these researches appeared considerably later than those of the Soviet investigators and are very speculative in nature.

This disregard of self-sticking in the investigation of the phenomena observed in gluing by polymeric compounds has no justification. Self-sticking has great importance theoretically, since it is connected with the structure of molecules. Investigation of it permits one to understand more thoroughly the nature of high-molecular substances. In addition, self-sticking has great practical importance. In a number of industries which use the operation, gluing is done by applying glue on the surface of the parts to be cemented together, allowing the parts to stand in air for some time for evaporation of the solvent, and then uniting them with or without pressure. It is obvious that self-sticking plays an important part in this gluing process.

Utilization of the property of self-sticking of polymeric substances forms the basis for the fabrication of rubber articles, the technology of a number of leather substitutes, the operations of gluing in the shoe and cardboard-box industries, etc. The same property plays a deciding role in the formation of films from dispersions of polymers, since for the formation of a continuous film on drying, adhesion must occur between the individual particles of the dispersion. It is understandable that in this case the phenomenon of self-sticking will be complicated by the presence, between the surfaces to be cemented together, of emulsifiers and other substances contained in the dispersion medium.

In the present research an attempt has been made to arrive at the nature of self-sticking of polymeric compounds on the basis of known experimental facts and modern views on the nature of these substances.

THE NATURE OF SELF-STICKING OF POLYMERIC SUBSTANCES

By self-adhesion (autohesion), we shall imply the ability of two contiguous surfaces of one and the same substance to give a sturdy connection preventing their separation at the place of contact.

In order that a substance may possess high self-adhesion it is necessary:

1. That the cohesional strength be adequate. This condition presents nothing new, since it must be observed also when high adhesive properties are required of any glue.

2. That at the contact of the two surfaces of the susbtance there must occur sufficient coalescence.

Essentially, the second requirement is fundamental: without sufficient coalescence self-adhesion cannot take place at all. Substances which are unable to coalesce (here belong the great majority of solid substances) have no self-adhesion capacity even though their cohesional strength may be very high. The second requirement seemed to contradict the fact that liquids which are able to coalesce completely have no autohesional strength. But in this case the low strength is explained not by the low autohesion but by the absence of cohesional strength in the liquids.

Polymeric substances are the only class of substances in which the combination of adequate cohesional strength and adequate capacity for coalescence is possible. Almost all of the glues in common use are polymeric materials.

How is coalescence brought about in the case of polymeric substances?

For the coalescence of two volumes of liquid the disappearance of the boundary of separation between these two volumes is sufficient. Because of the mobility of the molecules of an ordinary low-molecular liquid and the instantaneous establishment of intermolecular forces the area of contact of two portions of such a liquid ceases to be distinguished by its structure from any other part immediately after making contact.

For the complete coalescence of two pieces of a polymeric substance a single contact is insufficient. For realization of complete coalescence in this case, there must also occur, over a period of time, a reestablishment in the area of contact of the structure of the polymeric substance, that is, that interweaving of the high-molecular chains which is characteristic of any part in the volume.

The restoration of the structure of a polymeric substance in the area of contact, because of its enormous viscosity and the special form of the molecules, cannot take place by movement of whole molecules, such as occurs in the case of low-molecular liquids, but is accomplished by the diffusion of their individual parts. It is possible to conceive that in this case the terminal or middle parts of the molecular chains situated on one of the surfaces of the substance, in the course of thermal agitation, may penetrate into the superficial layer of the other part.

As a result of this phenomenon (which may also be called diffusion though not diffusion of whole molecules but of their individual ends or segments) there may be created a sufficiently stable bond between the two original portions of the polymeric substance so that it becomes evident in autohesional strength.

How a molecule, one end of which is situated in one layer of a polymer and the other end in another layer, realizes a sufficiently stable bonding of these layers still remains obscure to us. Josefowitz and Mark[4] believe that in this case the strength is caused by the retention of the ends of the molecules within the layer of polymer at the expense of intermolecular forces, but Penn[5] thinks
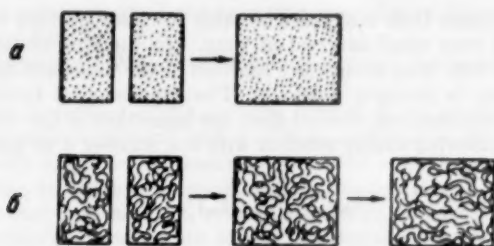
FIG. 1.—Diagram of the coalescence of low-molecular liquids, *a*,
and of polymeric substances, *b*.

that the phenomena of clogging and jamming (wedging) have great significance here.   It is very probable however that in the present case both of these factors may act simultaneously.

Everything that was said above concerning the nature of self-adhesion may be explained by Figure 1, in which coalescence in the cases of a low-molecular liquid and of a high-molecular substance is shown diagrammatically.

For self-adhesion of a polymeric substance viscosity is very essential.   On the one hand, it is perfectly obvious that the higher the viscosity, the more difficult and less complete will be the coalescence of the two surfaces brought into contact.   On the other hand however, the lower the viscosity, the easier it will be to sever the adhering surfaces because of the comparatively free move-ment of the molecules forming the bond.

It should also be pointed out that with sufficiently low viscosity the rupture of the sample may not take place at the plane of contact because of flowing of the polymeric substance.

Thus a high autohesional strength must obviously correspond to optimal viscosity.   Experiment showed that the viscosity of polymeric substances having high autohesion lies within the limits of 100–10,000 poises.

In the consideration of autohesion one often uses not viscosity but relaxa-tion time, a characteristic of the time required for the molecule of the given substance to change from its strained state caused by an external force to the unstrained state by rotation or shearing with respect to the molecules surround-ing it.

In Table I we are citing for illustration the viscosities and relaxation times of several substances[4].

Ordinary liquids, e.g., pentane or water, as one sees from this table, relax

TABLE I

COMPARISON OF VISCOSITIES AND RELAXATION TIMES

Substance	Viscosity (poises)	Relaxation time (sec.)
Pentane	10^{-2}	10^{-14}
Water	2×10^{-2}	10^{-13}
Olive oil	1	10^{-12}
Glycerol	2×10^{1}	10^{-10}
Heavy motor oil	10^{2}	10^{-10}
Spinning solns.	$10^{2} - 10^{5}$	10^{-9}
Mixtures for die casting	2×10^{4}	10^{-7}
Molten glass	$10^{5} - 10^{6}$	10^{-5}

very quickly because their molecules are able to rotate or shift with respect to each other in a very small interval of time. In the case of large molecules, especially those with long chains, the reaction of the molecules to the action of an external force is strongly delayed. The experimental investigation, like the theoretical calculations, showed that the logarithm of the viscosity is connected by the following simple relation with the number n of monomeric units in the chain:

$$\log \eta = a + bn^{\frac{1}{2}}$$

For long chains ($n > 100$) the first term on the right hand side of the equation may be disregarded and the logarithm of the viscosity becomes directly proportional to the square root of the degree of polymerization. Thus the equation cited above indicates a very rapid increase of viscosity, and hence also of relaxation time, with increasing chain length. Thus a substance having chains consisting of 1000 units, for example, has in the fused state a viscosity approximately 1000 times as high as that of a substance with chains of 100 units.

Substances with a degree of polymerization $n = 50$–300 and a relaxation time varying from 10^{-7} to 10^{-4} second ordinarily have good self-adhesion.

Closely related to the nature of the autohesion and coalescence of polymeric substances is the question of how to measure both of these quantities.

We believe that the most acceptable measure of the autohesional strength is the force one must apply for the rupture of two plane surfaces of the given substance that have been brought into contact. It is also expedient to speak of autohesional strength only in case the rupture takes place in the plane of the original contact. If this condition is not observed and the sample is broken in another place, this means that the autohesional forces attain the values of the cohesional ones and the results obtained should be called the cohesional strength of the given material.

As a measure of the coalescence of polymeric substances one may use the ratio of the autohesional strength to the cohesional. When the autohesional strength attains the values of the cohesional strength, the degree of adhesion obviously becomes equal to unity. This means that such complete adhesion of the two pieces of the given substance occurred that the structure at the contact does not differ from the structure of the substance in other parts of the volume.

It is natural that the conditions of measurement and the previous history of the pieces to be separated may exert a strong influence on the autohesional strength and degree of adhesion measured by these methods. Consequently, in order to obtain comparable results the experimental conditions must be strictly controlled.

INFLUENCE OF VARIOUS FACTORS ON SELF-ADHESION

Starting from the point of view adopted above with regard to the nature of self-adhesion, it is perfectly understandable that the manifestation of autohesion must be promoted by all of the factors which accelerate and facilitate thermal agitation: increase of temperature, introduction of softeners (plasticizers) and solvents and the like.

On the other hand, a negative influence on autohesion would be exerted by all factors which inhibit such agitation: lowering of the temperature, orientation of the chain molecules in the layer of polymeric substance as a result of stretching or conditions of preparation, introduction into the molecule of polar groups,

interlacing of the chains during vulcanization or oxidative structure formation (structuring) and the like.

Let us consider the influence of certain factors on the autohesion a little more closely.

The duration of contact of the surfaces influences the results of the determination of autohesive strength and degree of coalescence of polymeric substances in a very fundamental manner, since the coalescence, which has a diffusional nature, as we saw, proceeds as a function of time.

Taking this fact into account, it is expedient to characterize the self-adhesion of a polymeric substance not by the autohesive strength after a certain, often even unstandardized length of time elapsing from the moment of making contact, but by all of the kinetic curves describing the variation of the autohesive strength as a function of time.

In Figure 2 are shown a number of such kinetic curves obtained by Margolina for various rubbers. In elucidation of the data which are cited it should be pointed out that the autohesive strength in this case was found by deter-
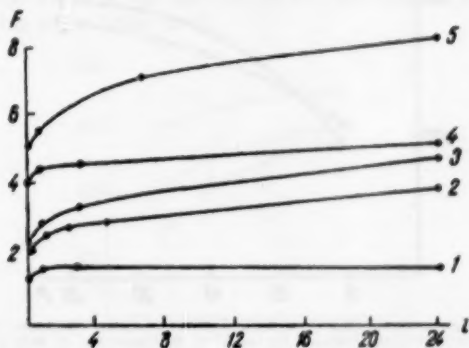
Fig. 2.—Kinetics of laminating. Ordinage: F, resistance to shear, kg./cm.^{2}. Abscissa: t, time, hrs. *1*. Butadiene-Na rubber. *2*. A synthetic rubber. *3*. Polyisobutylene. *4*. Natural rubber. *5*. The synthetic rubber of Curve 2 after treatment.

mination of the resistance to shear of doubled-over (overlapped) strips of fabric on the working surface of which the same quantity of rubber was applied before the doubling. It is natural that the results were considered characteristic of the autohesive strength only when the separation of the two strips of fabric took place at the rubber. In all cases, as may be seen from Figure 2, the dependence of the autohesive strength on the duration of the contact is expressed by a curve having a parabolic form. This agrees well with the fact that self-adhesion has a diffusional character. In individual cases duration of contact of the joined samples up to 24 hours gives a 60–100 per cent increase of strength of the splice.

Under concrete conditions of the coalescence of two similar surfaces of a polymeric substance, with provision for complete contact, a minimal time must exist, after which the degree of coalescence practically reaches its limit. In individual cases the degree of coalescence may at the same time attain unity. This "critical" time, established under certain conditions, must be characteristic for each polymeric substance and must depend on the intensity of the thermal motion of individual members (links) or ends of the chain molecule of this sub-

stance. The form of the curves obtained by Margolina completely confirms the existence of this critical time.

It is very important to note that the kinetic curves of self-adhesion shown in Figure 2 are reproducible and perfectly characteristic for the various polymeric substances. In the case of natural rubber Curve 4 has a steep rise and the autohesive strength all at once attains high values which in general agree excellently with the idea of self-adhesion of natural rubber which we have from practice. Curve 3 for polyisobutylene has a much less steep rise. Curve 1 for synthetic butadiene-sodium rubber attains its maximum very promptly, but the absolute value of the autohesive strength in this case is very small. In Figure 2 one also sees a sharp difference in the form of the kinetic curves and in the maximum autohesive strength for one of the synthetic rubbers and for the same rubber which has undergone special treatment.

All of this again confirms the expediency of characterizing the self-adhesion of the various polymeric substances with the aid of kinetic curves.
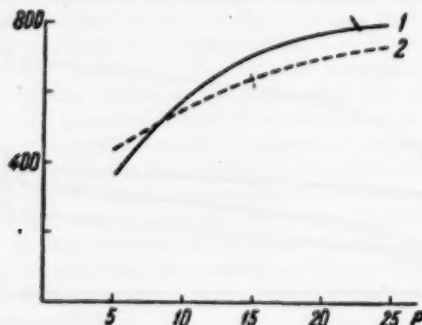
FIG. 3.—Effect of pressure on the autohesive strength of rubber mixtures. Ordinate: Resistance to separation, g./cm. Abscissa: Pressure, kg./cm.². 1. Soft mixture. 2. Stiff mixture.

Data on the influence of time of contact of two layers of a rubber mixture, for synthetic butadiene-Na rubber, on the strength of their adhesion are also cited by Priklonskaya in her article[2]. In this article it is shown that the duration of compression may partially compensate for the amount of pressure to which the two layers were subjected after they were brought into contact and, inversely, with large pressures the duration of the compression may be diminished. These results confirm completely our view that self-adhesion has a diffusional character.

Pressure for the accomplishment of self-adhesion is essential only for guaranteeing close contact of the two coalescing surfaces, which is attained at the expense of either elastic or plastic deformations of the irregularities on the surfaces of the layers. An increase of pressure above that which is necessary for complete contact of the two surfaces cannot lead to an increase of autohesion. The existence of such a pressure limit is excellently illustrated in Figure 3, which is taken from the article by Priklonskaya[2].

Two raw rubber mixtures, prepared with coreless butadiene-Na rubber having a plasticity of 0.38, were taken for the analysis, and one of the mixtures was made more plastic by addition of a softener. The compression of the laminated samples was carried out at different pressures for 15 minutes, after which the samples were separated on the dynamometer. The data shown in

Figure 3 indicate that as the compression pressure is increased the resistance to separation tends toward a definite limit. With large pressures the surface of the samples after separation is roughened, for here the rupture proceeds even through the rubber mixture as a result of complete coalescence.

It is interesting to note that the greatest resistance to separation was observed in the case of the most plastic mixture. This may be explained merely by the fact that in this case, because of the smaller stiffness of the mixture, and consequently because of the greater mobility of the molecular chains, coalescence took place more completely. For a stiffer mixture one could probably obtain the same autohesive strength by increasing compression time.

It is perfectly obvious that the smoother the surfaces, the smaller is the pressure that must be applied to attain close contact. At the same time it should be recalled that the formation of a close contact is influenced by the rheological properties of the material and in particular by its capacity for flowing under small loads. Scott[7] attaches exceptional significance to the latter circumstance and explains the great difference in the self-adhesion of natural rubber and of GR-S rubber, for example, by the fact that the latter is much less capable of flowing under small loads.
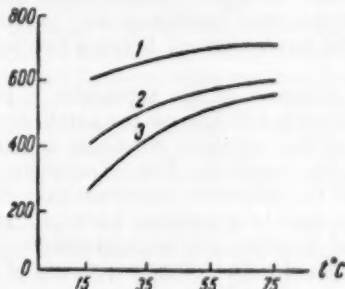
FIG. 4.—Effect of temperature on the autohesive strength of rubber mixtures. Ordinate: Resistance to separation, g./cm. Abscissa: Temperature, ° C. 1. Pressure, 20 kg./cm.². 2. Pressure, 5 kg./cm.². 3. Pressure, 3 kg./cm.².

In estimating the ability of polymeric substances to flow one must not forget that the mechanical properties in the surface layer may be entirely different from those in bulk. This circumstance may make it necessary to apply, for bringing the two surfaces into contact, loads that are entirely different from those calculated.

In the case of thermoplastic polymeric substances temperature influences self-adhesion in the strongest manner, for with increase of temperature the intensity of the thermal agitation increases. If the substance is able to melt, then by raising the temperature it is always possible to make the degree of coalescence equal to unity. In that case the autohesive strength must equal the cohesive strength of the material.

It should be noted that a rise of temperature also improves the contact between the surfaces, since the forces inhibiting the deformation of the polymeric substance, as a rule, decrease on warming.

The influence of temperature on autohesive strength (resistance to separation) at different compression pressures for samples of crude rubber mixtures prepared from coreless butadiene-Na rubber with a plasticity of 0.38 is shown in Figure 4, which is copied from the article of Priklonskaya. Pressing of the

samples before separation was done under pressures from 3 to 20 kg./cm.[2]   The influence of temperature, as one sees from this figure, is expressed more strongly at small pressures.   This is evidently connected with the fact that as a result of the rise of temperature the mixture becomes more plastic, which guarantees good contact of the surfaces even with small pressure.   It is also interesting that the effect of heating is expressed for the most part up to temperatures of 45–50°.   We are inclined to explain this by the fact that with the compression time adopted a temperature of 45—50° guarantees complete coalescence of the two samples of the rubber mixture.

One should distinguish between the effect of temperature during contact of two pieces of a polymeric substance and its influence at the moment of determination of the strength of the splice.   In the latter case the autohesive strength falls, since heating, which leads to increased intensity of thermal agitation, will increase the gliding of the molecules and weaken the bond created with their aid between the two pieces of the polymeric substance.

Introduction of a softener improves the coalescence, since the molecules of the softener shield the centers of application of the intermolecular forces and thus promote the thermal movement which is indispensable for the adhesion of the surfaces.   At the same time, softeners may lower the autohesive strength, since by exhibiting intermolecular lubrication they promote the sliding of the molecules and weaken the bond produced between two layers of the polymeric substance.

Thus the action of softeners on the autohesion is two-fold.   Whether a softener, all things considered, will increase the autohesive strength or lower it depends on the nature of the polymeric substance and the softener, the proportion of softener, and the conditions of its introduction.

In case the chains of the polymeric substance have sufficient mobility the introduction of softener may be considered harmful.   If the polymeric substance can be crystallized, however, or if large intermolecular forces act between its chains, the introduction of not too large a quantity of softener, as a rule, is useful.

The possibility of different actions of a softener on the autohesion of a rubber mixture is clearly shown in the article by Priklonskaya[2].   On introduction into stiff rubber mixtures of a reclaimed rubber containing a softener the capacity for self-adhesion was increased.   But introduction into the mixture of considerable quantities of softener led to a lowering of self-adhesion.

The nature of the softeners introduced must unconditionally exert a very strong influence on the capacity of a polymeric substance for self-adhesion. Unfortunately, we still have very few data on this question, and here we must confine ourselves merely to very general considerations.

True softeners are able to solvate the molecules of the high polymer well, and they also increase the diameter of the molecular chain and decrease its deflectivity.   Both of these circumstances, it would seem, must exert a negative influence on the diffusion power of parts of the molecule.   At the same time, true softeners, on being adsorbed on the chain molecules, permeate between the individual chains and thus "loosen" the structure of the polymer, which unconditionally must promote the diffusion.

Pseudo-softeners, however, do not cause such a loosening, but accumulate in the microcavities formed between the molecules.   Moreover, a polymer, which behaves toward the pseudo-softeners as toward foreign bodies, will tend to force them out to the surface.   It is natural that the presence of a layer of exuded low-molecular softener must have an unfavorable effect on self-adhesion.

Which of the above-mentioned factors will predominate in each concrete case is difficult to state without special experiments. On the basis of the existing observations, however, it may be believed that true softeners increase the self-adhesion to a great extent. Thus according to the data of Margolina, who investigated the influence of the addition of 10 per cent of rosin on the properties of one of the synthetic rubbers, the capacity of this rubber for self-adhesion increased somewhat. On introduction of 10 per cent of vaseline oil, however, which does not appear to be a true softener for the same rubber, the self-adhesion was lowered.

Solvents exert an influence on the coalescence of surfaces similar to the effect of softeners. But because of the ability of solvents to become volatilized they are unable to exert an unfavorable influence on self-adhesion. Gluing by renewal of the surface of the adhesive film by solvent, as known in technology, is an example of the use of the favorable action of the solvent on coalescence.

The effect of smearing with weak cement solutions the two surfaces of the rubber mixture that are to be joined together in the fabrication of rubber articles should also be ascribed, to a great extent, to the ability of the solvent to loosen up the surface of the mixture and promote the thermal motion of the links (chain members) or ends of the molecules.

In conclusion of all that has been said concerning the effect of softeners and solvents, it should be pointed out that, according to the data of Maslovskiĭ and Popova[2], solvents of different kinds (aviation gasoline, benzene, toluene, carbon tetrachloride, sulfuric ether) act approximately the same way on the self-adhesion of synthetic butadiene-Na rubber. This may be explained by the fact that all of the solvents dissolve the rubber sufficiently and therefore give approximately the same effect in the sense of opening up the structure of the polymer.

Fillers, unlike softeners and solvents, always lower the autohesive strength of rubber. Active fillers lower the self-adhesion because the molecules of the polymeric substance are adsorbed on their particles and therefore lose their mobility. Inactive fillers must lower the autohesive strength because, per unit of total area of contact of the two samples, there is a smaller area of direct contact of the polymer.

INFLUENCE OF THE FORM AND SIZE OF THE MOLECULE ON THE SELF-ADHESION OF A POLYMERIC SUBSTANCE

Since the complete coalescence essential for good self-adhesion is caused by the thermal movement of the individual parts of the molecules, the chemical nature of the substance, which determines the mobility of the links of the molecular chain, shows the greatest influence on self-adhesion. Here belong the nature of the atoms from which the skeleton of the molecule is constructed, the presence in the molecule of polar groups, etc.

Excellent self-adhesion may be observed only in a polar or weakly polar high polymers. In the case of polar high polymers, because of the action of intermolecular forces preventing the intensive movement of the links of the molecule, the ability for self-adhesion is destroyed. Albumen and nitrocellulose may serve as examples of this. But in the presence of a sufficient quantity of solvent or softener self-adhesion may be developed also by substances with polar molecules, since the solvent or softener shields the centers of intermolecular attraction and therefore guarantees the possibility of thermal motion.

Excellent self-adhesion is observed only in amorphous substances, since in

crystalline compounds the chains are arranged in a certain order which does not permit the individual parts of a chain to perform a sufficiently intensive thermal agitation. An example of such substances is paraffin. In spite of the apolarity of paraffins, which would seem to guarantee the appearance of autohesion, paraffins are usually capable of being crystallized and therefore do not have self-adhesion.

It is apparent that on raising the temperature self-adhesion may be developed also by crystalline substances which can be melted. The same paraffins, which develop autohesion within known limits of temperature, are an example.

The form of the molecules must also exert a strong influence on self-adhesion, since it is determined by the capacity for thermal movement of the individual parts of the molecule. Molecules with long branches probably provide conditions for increased self-adhesion, since such molecules, in the first place, are firmly mounted in the layer of substance and, secondly, they have many ends capable of diffusing into the depth of the high polymer.

Mark[8] records a positive influence of branching of the molecules on the adhesive properties of a polymeric substance.

TABLE II

EFFECT OF PLASTICITY ON ADHESION

Plasticity of the rubber from which the adhesive was prepared	Resistance to separation (kg./cm.)
0.47	0.3
0.26	0.65
0.23	1.06
0.21	2.20
0.14	2.00

Molecules with a large number of short branches have lowered self-adhesion, since these short branches, because of steric reasons, will naturally impair the ability of the molecular chains to diffuse into the depth of the polymeric substance.

Finally, the dimensions of the molecule, on which its mobility as a whole depends, cannot fail to influence self-adhesion. Unfortunately, the question concerning the influence on self-adhesion of the length of the molecule cannot at present be discussed definitely. On the one hand, the longer the molecular chain, the smaller on each of the joined surfaces is the number of free ends which can penetrate into the depth of the adjacent layer of polymer. On the other hand, the longer the molecular chain, the more difficult for it to be separated from the total mass of high polymer and the greater will be the strength of the union of the two pieces of the latter after a certain time of contact.

Some investigators[9] assume that only the free ends of the molecules are capable of diffusion. But we consider it more probable that portions of the middle sections of the molecule are also able to take root in the depth of the polymer. A number of other authors also adhere to this view [4,10,11]. In that case, if a molecule is sufficiently flexible to form long loops along its length, the adhesive strength must be increased with the length of the molecule, for here the phenomena of wedging can occur besides the penetration of the loop between the molecules of the polymer[5].

An increase of autohesion with increase of the length of the molecule is indicated by the data of Maslovskiĭ and Popova[13], who determined the adhesiveness

of synthetic butadiene-Na rubbers of different plasticity. The conditions for preparation of the samples for separation were as follows: a 10 per cent solution of synthetic butadiene-Na rubber was placed on a strip of calico and then dried; the dry surface of the adhesive film was moistened with the solution; the strips were put together with the rubber adhesive inside, flattened with a roller, thoroughly dried, and separated on the dynamometer after 12 hours. The results obtained are shown in Table II.

From this table one sees that the lower the plasticity of the rubber, the higher is the autohesion. These data show the increase of autohesion with increase of molecular weight, since the increase of molecular weight with decrease of the plasticity of butadiene-Na rubber is generally known[12].

A certain contradiction to the views we have expressed, that an increase of chain length provides conditions for an increase of autohesion of polymers, exists, apparently, in the observations on the increase of the adhesiveness of rubber through degradation by oxygen or otherwise. Actually, there is no contradiction here.

By degradation as a result of the breaking up of the molecular chains into a number of sections the number of ends capable of diffusion is actually increased. But simultaneously, as the molecules of smaller length may be separated more easily from the total mass of high polymer, one observes a change of its mechanical properties, diminution of the cohesive strength and increase of the viscosity component in the complex of its elastic-viscous properties.

SELF-ADHESION OF VARIOUS POLYMERIC SUBSTANCES

On the basis of the ideas presented above, the self-adhesion of most rubbers and of certain other polymeric substances can be explained more or less satisfactorily.

The views expressed at various times to the effect that the self-adhesion of rubber may be determined to a certain extent by the presence in it of albumins[12] or resins[13] have failed to withstand serious criticism.

Now it is perfectly clear that natural rubber has a high autohesion only because of the chainlike form of its molecules and the absence of polar groups in them. The presence in the molecules of natural rubber, which have a *cis*-configuration, of short side groups (methyl groups) cannot have any noticeable effect on the ability of the links of the molecule to diffuse into the depth of the layer of polymeric substance, but prevents the crystallization, which guarantees the possibility of the appearance of self-adhesion. In gutta-percha however—a stereoisomer of rubber with *trans*-configuration of the molecule—because of its ability to crystallize, self-adhesion at ordinary temperature is absent.

In such derivatives of natural rubber as chlorinated rubber, autohesion is absent because of the presence in the molecule of several atoms of chlorine. But chlorinated rubber, like gutta-percha, if softened, acquires elastic properties, and exhibits self-adhesion on increase of temperature to 70°, namely when the effect of the temperature predominates over the effect of the molecular forces caused by the presence of polar atoms in the molecule.

Synthetic chloroprene rubber, like natural rubber, has a high self-adhesion. The presence of infrequent branchings, characteristic for this polymer[14], would promote self-adhesion of the chloroprene rubber even more. But the presence in the molecule of one atom of chlorine causes the appearance of intermolecular forces, and therefore chloroprene rubber usually lacks somewhat as compared to natural rubber with regard to autohesion.

Synthetic butadiene-Na rubber has poor self-adhesion because of the comparatively small length of its molecules. We have seen above, from the data of Maslovskiĭ and Popova, how strongly an increase of molecular weight guarantees the autohesive strength of butadiene-Na rubber. Furthermore, this rubber has poor self-adhesion because of the presence in its molecule of a large number of vinyl groups which prevent, for purely steric reasons, the diffusion of the links or ends of molecules from one layer of high-polymer to the other.

The ordinary copolymers of butadiene and styrene have self-adhesions close to the self-adhesion of butadiene-Na rubber.

In general, it should be pointed out that the self-adhesion of the copolymer of butadiene and styrene depends strongly on the content in the initial mixture of monomers of the vinyl component. A certain increase of self-adhesion of GR-S rubber in comparison with pure butadiene rubber, which is observed for copolymers with a small styrene content, is evidently explained by the fact that a small quantity of a vinyl compound promotes the polymerization of the butadiene in the 1,4-position. The lowering of the self-adhesion of GR-S rubber on further increase of the proportion of styrene is explained, in our opinion, by the presence, in the molecular chains that are formed, of a large number of short branches consisting of benzene rings. This explanation of the self-adhesion of the butadiene-styrene polymers is entirely different from the ideas of Josefowitz and Mark[4] and also of Penn[5], who considered the presence of transverse bonds (crosslinkages) between the molecules as the reason for the low autohesion of GR-S rubber. Our opinion seems to us better grounded, for if these authors were correct, then the capacity for self-adhesion of the copolymers would increase with increasing styrene content, since with increase of the content of the vinyl component the probability of formation of crosslinkages would decrease.

Copolymers of butadiene and styrene exhibit an increase of self-adhesion with rise of temperature[15]. Moreover, just like pure butadiene synthetic rubber, the copolymers of this type give no increase, and even display a certain decrease, of self-adhesion on mastication or oxidation. The reason for this is probably the formation, under the action of atmospheric oxygen, of crosslinkages between the chain molecules of the polymer. Copolymers of butadiene and acrylonitrile exhibit poor self-adhesion, evidently because of the presence of polar nitrile groups in the molecule.

Polyisobutylene has high self-adhesion because of its chain structure, the absence of branches, and the complete non-polarity of its molecules. The presence of methyl side groups, as pointed out above, cannot appreciably affect the diffusion capacity of the links of the molecules, but removes the possibility of crystallization. In complete accordance with this, polyisobutylene exhibits perfect elasticity and capacity for self-adhesion even at $0°$ C. Polyethylene, however, has at ordinary temperature no self-adhesion power, in spite of the complete apolarity of the molecule and the absence of any branches. The reason for this is the peculiar tendency for crystallization of the zigzag-shaped molecules of polyethylene. This is confirmed also by the high softening temperature of polyethylene, $115°$ C.

All of the vulcanized rubbers have no appreciable self-adhesion. This too is understandable. The spatial structure of the molecules prevents the diffusion of their links into the layer of polymer. Cellulose and its esters in the undissolved or unmasticated form have no autohesion because of the polarity of the molecules and the high intermolecular forces connected therewith. Swelled gels of these substances, when the intermolecular forces are weakened

by the shielding effect of the solvent molecules, have high self-adhesion.   The same can be said of albumins.   In the dry form, casein displays complete absence of self-adhesion.   But concentrated solutions of casein have excellent autohesion, and in this form, as is known, casein is a valuable adhesive.

What has been adduced above suffices, in our opinion, to show how fruitful the application of modern ideas concerning the structure of polymers may be for explaining self-adhesion, and also for solving problems of adhesion in general.

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SELF-ADHESION (AUTOHESION) OF
POLYISOBUTYLENE. II *

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In accordance with our concepts[1], the autohesion of polymers is caused by diffusion of segments of chain molecules from one layer into another layer of the same polymer brought into contact with the first. This conclusion was drawn by us from generally known facts and modern concepts concerning the nature of high-molecular substances. The present work represents an attempt to confirm experimentally the diffusional theory of autohesion.

Polyisobutylene with a molecular weight of 150,000 was used to investigate autohesion. Polyisobutylene was chosen as the material for study because its molecules contain no double bonds. This renders them sufficiently stable in regard to oxidation at ordinary temperature.

The strength of autohesion was characterized by the stress necessary to delaminate two laminated fabric strips treated before laminating with the polymer solution. For the preparation of splices subjected to delamination in determining the autohesion of polyisobutylene, use was made of strips of unsized technical cotton fabric with a smooth surface. The working length of the specimen was always 10 cm.; its width was usually 5 cm. The polyisobutylene was applied to the specimens in the form of 6.0–7.5 per cent solution. The polyisobutylene solution was made up in a low-boiling fraction of aviation gasoline, which left no dry residue upon evaporation. The quantity of polyisobutylene, in grams per square centimeter of specimen surface was established from the weight of the absolutely dry initial fabric and of the polymer coated material after drying.

The fully dried specimens were laminated by putting them together with the polyisobutylene coated surfaces facing each other and holding the resulting splice at a definite temperature, for a definite time, under a metal plate of known weight, 5×10 cm. in size, which supported a known load.

The specimens were delaminated on as pecial dynamometer constructed in the Central Scientific Research Institute of Leather Substitutes. The delamination rate was regulated by changing the number of turns of a pilot wheel per unit time. An automatic recording device made it possible to obtain a diagram of the delaminating stress plotted against the length of the specimen, from which the strength of autohesion in g./cm. could be calculated.

In determining autohesion, the surface character of the delaminated specimens was always carefully checked. Use was made of the results of those determinations in which the polymer coated specimen surface after delamination was perfectly smooth. This condition indicated that the delamination occurred at the contact surface between the two polymer layers, and that what was determined was, in fact, autohesion.

Fig. 1.—Effect of quantity of polymer applied to fabric upon resistance to delamination. Ordinate: Delamination resistance, g./cm. Abscissa: Amount of polymer, g./cm².

Already the first experimental data showed that the resistance to delamination increases with increasing rate of delamination, the curves bearing a clearly expressed parabolic character. Subsequently, to eliminate the influence of the rate of delamination upon the experimental results, delamination was always carried out at one and the same nominal rate of 0.27 cm./sec.

Inasmuch as it was found that the resistance to delamination depends upon the thickness of the polymer layer applied to the fabric, this dependence was investigated in more detail. The experiments were conducted with different quantities of polyisobutylene applied per square centimeter. The time of contact in laminating was 5 minutes; the pressures was 0.04 kg./sq. cm.; lamination and delamination were performed at room temperature, 22° C.

The results obtained are presented graphically in Figure 1. As may be seen, the resistance to delamination at first increases as the quantity of polymer per square centimeter increases, but then remains constant after the quantity of polyisobutylene reaches approximately 0.025 g./sq. cm. This indicates that, with such application, the base fabric no longer affects autohesion. Subsequently, all experiments were conducted with specimens containing no less than 0.025 g. of polymer per square centimeter.

Interest attached to clarifying whether autohesion experiences a change upon repeated lamination and delamination of one and the same specimen. For this, fabric strips with polyisobutylene applied to them were laminated as usual, held for 5 minutes under load, were delaminated on the dynamometer, were laminated again, etc., for 10 cycles. For the rest, the experimental

Fig. 2.—Effect of contact time on resistance to delamination. Ordinate: Delamination resistance, g./cm. Abscissa: Contact time, hr.
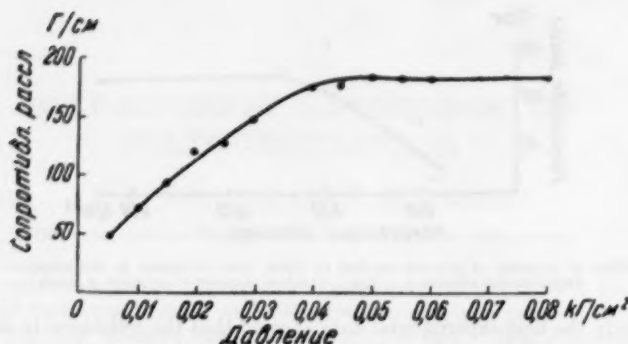
Fig. 3.—Effect of contact pressure on resistance to delamination.   Ordinate:
Delamination resistance, g./cm.   Abscissa: Pressure, kg./cm.²

conditions were the same as in the preceding series.   The results showed that,
upon repeated successive delaminations, the polymer coated specimen surface
remains smooth after delamination, and that the curve of resistance to de-
lamination plotted against specimen length retains the same form.   This
confirms the fact that delamination proceeds at the initial contact surface and
indicates the reproducibility and significance of autohesion-strength deter-
minations.

Experiments were thereupon carried out to clarify the influence of contact
time upon the strength of autohesion.   In these experiments, the contact pres-
sure was 0.04 kg./sq. cm., and the lamination and delamination temperature was
22° C.   The results of the determinations are presented in the form of curves
in Figure 2.   As may be seen, the resistance to delamination increases along a
parabolic curve with increasing contact time.

To clarify the effect of contact pressure between the polymer surfaces upon
the strength of autohesion, experiments were carried out in which the pressure
under which the splice was held under load was varied.   The contact time was
5 minutes, the temperature 22° C.   The data obtained are presented graphic-
ally in Figure 3.   As may be seen, the resistance to delamination increases as
the pressure increases to 0.04 kg./sq. cm., whereupon it remains constant as the
pressure increases further.

Finally, to clarify the effect of temperature upon the strength of autohesion,
experiments were carried out in which the temperature of the splice when under
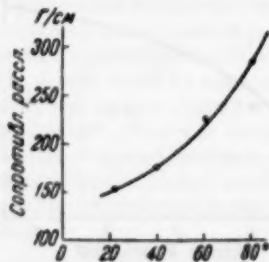
Fig. 4.—Effect of laminating temperature on resistance to delamination.   Ordinate:
Delamination resistance, g./cm.   Abscissa: Temperature, ° C.

pressure was varied.   This was realized by simply holding the splices in a thermostat at the temperature required.   After being held for 5 minutes in the thermostat under a pressure of 0.04 kg./sq. cm., the splices were cooled, held for 30 minutes at room temperature, and only then subjected to delamination. The results of delamination of the specimens are presented graphically in Figure 4.   As may be seen, the resistance to delamination rises with increasing contact temperature along a curve possessing an exponential character.   It is important to note that specimens laminated at a temperature of 100° C and higher could not be delaminated, since the delaminating load would have exceeded the load limit of the dynamometer.

The results of the above-described experiments fully confirm our previously expressed opinion that autohesion possesses a diffusional character.

The increase in resistance to delamination with increasing rate of delamination is quite comprehensible from this point of view, since a certain time is required to permit the long-chain molecules of the two layers being delaminated to become disentangled and separated.

The increase in resistance to delamination with increasing contact time along a parabolic curve also indicates that autohesion is diffusional in nature.   It can be assumed that, as a limiting condition, at greater contact times, the resistance to delamination must reach values corresponding to the rupture of the polyisobutylene itself.   Unfortunately, in order to confirm this hypothesis experimentally, it is necessary to determine the tear resistance of polyisobutylene itself, which is a difficult task in view of its tendency to flow.

An increase in the pressure of the system cannot increase the rate of diffusion.   This, as we have seen, is in fact confirmed by experiment.   A certain pressure is in this case needed merely to bring the two polymer layers into contact with each other.   Evidently, the pressure of 0.04 kg./sq. cm. was in our case that pressure which ensured complete contact.   It is obvious that this critical pressure can vary depending upon the elastoplastic properties of the polymer, as well as the uniformity of application of the polymer upon the fabric base.

The effect of temperature upon autohesion is most revealing.   As we have seen, the resistance to delamination sharply increases with increase in the temperature at which the two surfaces were in contact.   This must be explained by the intensification of diffusion as a result of the increase in the thermal motion of the molecular segments.

Knowing the dependence of the resistance to delamination upon the contact temperature, and assuming that the strength of autohesion is a measure of how deeply the segments of the long chain molecules have mutually diffused into each other during the contact period, it is not difficult to calculate the activation energy of autohesion with the aid of the known equation of Arrhenius:

$$p = p_0 e^{-E/RT}$$

where p is the resistance of the splice to delamination, p_0 is a constant, E is the activation energy of the process, R is the gas constant, and T is the absolute temperature.

The corresponding value of E, as calculated from the data of Figure 4, is 2800 cal.   This quantity is characteristic of the energy of activation of diffusional processes.

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EFFECT OF MOLECULAR WEIGHT, SHAPE OF THE MOLECULE, AND PRESENCE OF POLAR GROUPS ON THE AUTOHESION OF HIGH POLYMERS. III *

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In our previous papers we formulated a concept of autohesion of high polymers as a diffusion process[1], and presented a detailed study of the effects, on the autohesion of polyisobutylene, of the rate of separation of the contacting polymer surfaces, contact pressure, time, and temperature of contact[2]. The object of the present study was to determine the effect of molecular size and shape, and also of the nature of the polymer, on the autohesion of high polymers.

The quantitative evaluation of autohesion of high polymers was carried out by the technique used successfully in our earlier studies.

In this technique the autohesion was determined by the force needed to separate two doubled strips of fabric, which were coated with the polymer in a volatile solvent before laminating. Complete evaporation of the solvent from the polymer was always carefully ensured before laminating. The laminating was always effected under the same conditions, established in our previous study[2]. The quantity of polymer on the fabric was never less than 0.03 g./sq. in., and the pressure in laminating was 40 g./sq. cm. The only factors to be varied, according to the aim of the experiment, were the time during which the layers of rubber were in contact, and the temperature during contact.

The separation of the splices was carried out on a Central Research Institute for Leather Substitutes dynamometer with jaws which separate in a horizontal direction at a constant rate of 0.27 cm./sec. The dynamometer was fitted with an automatic recording device. From the diagrams obtained it was possible to determine the average resistance to separation and to calculate the work of autohesion from the formula:

$$Au = \frac{p2gl}{lb} = \frac{2pg}{b}$$

where p is the mean force of separation; l is the length of the working section of the splice; b the width of the splice; and g the acceleration due to gravity.

The nature of separation of a splice was in each case carefully checked. Only those values of the work of autohesion were accepted which corresponded to a perfectly smooth surface of the layers of polymer on both strips of fabric after separation. If these surfaces were rough or if the polymer became detached from the fabric, the value measured was clearly not the autohesion but the cohesional strength or the adhesion of the polymer to the fabric.

Effect of molecular weight on the autohesion of high polymers.—Samples of polyisobutylene with molecular weights of 20,000, 100,000, 150,000, and 200,000 were used for the experiments. In this series of experiments the polymer was applied to the fabric strips from benzene solution. Figure 1 shows the data on changes in the resistance to separation and the corresponding work of autohesion with changes in the duration of contact of the polyisobutylene layers.

It must be noted that in the case of polyisobutylene with molecular weight 20,000, separation by the initial contact method was observed only for relatively small contact times. When the contact time exceeded 1 hour, the polymer surface on the fabric strips after separation was rough. This indicated that in this case the cohesional strength of the polymer was determined.

As is seen from the shape of the kinetic curves, the resistance to separation and the work of autohesion in all cases increases with increasing time of contact, and tends to a definite limit. The rate of increase of autohesion is greater for lower molecular weights of polymer, that is, for shorter molecules. Since the
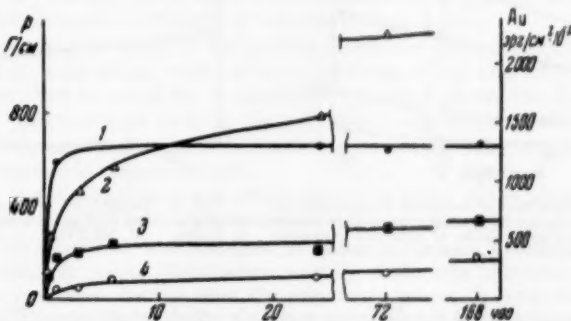
Fig. 1.—Effect of contact time on the resistance to separation, p, and work of autohesion, Au, for polyiso-butylenes of different molecular weights: *1.* 20,000. *2.* 100,000. *3.* 150,000. *4.* 200,000.

mobility of segments of isolated long chain molecules does not depend on the molecular weight for degrees of polymerization in excess of 15–20, the results indicate that the autohesion of high polymers of sufficiently high molecular weight is largely due to the diffusion of the ends of the chains.

The results obtained do not permit any definite conclusions to be drawn concerning the limit of autohesion of the different polymers, corresponding to the cohesional strength of the material. However, the shape of the curves does not contradict the generalization that the cohesional strength of a polymer increases with molecular weight. In particular, from the curve for the polymer with molecular weight 200,000 it seems likely that the maximum value of the autohesion, which is reached far beyond the limits of the diagram, will be greater than the maximum autohesion for all the other polymers. The curve for the polymer of molecular weight 20,000 is of interest. It is seen that this curve reaches its limit, which corresponds to 670 g./cm., in a contact time of the order of 1 hour. This is in full agreement with the fact that when laminated strips which have been in contact for more than 1 hour are separated, the surface of the polymer layer is rough. Evidently, in that case the cohesional strength of the polymer was determined.

Figure 2 shows changes of the resistance to separation and of the work of

autohesion of polyisobutylenes of different molecular weights with variations of temperatures of contact.   The contact time in this series of experiments was 5 minutes.   It is seen that the curves are exponential in nature.   This confirms that autohesion is diffusional in character.   As we know, an exponential dependence of diffusion rate on temperature is found also in low molecular substances[3].

With a knowledge of the dependence of autohesion on the contact temperature, and on the assumption that the resistance to separation is a measure of the depth to which the segments of the chain molecules diffused during contact, it is easy to calculate the activation energy of autohesion.   This is the energy re-
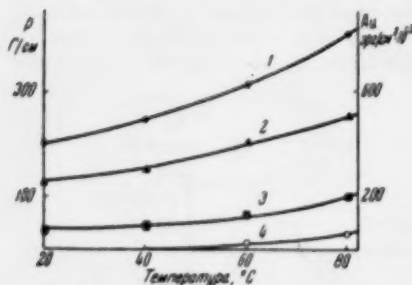
FIG. 2.—Dependence of resistance to separation, p, and work of autohesion, Au, on temperature during contact for polyisobutylenes of different molecular weights: _1._ 20,000.   _2._ 100,000.   _3._ 150,000.   _4._ 200,000.
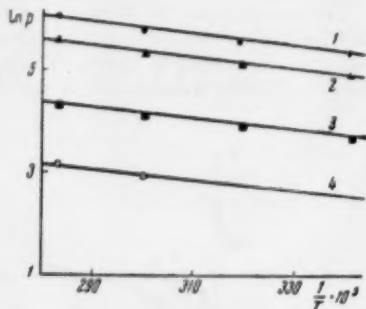
FIG. 3.—Dependence of ln p on $1/T$ for polyisobutylenes of different molecular weights: _1._ 20,000.   _2._ 100,000.   _3._ 150,000.   _4._ 200,000.

quired for a segment of the diffusing molecule which constitutes a kinetic entity to enter a gap between the molecules of the layer into which it diffuses, and to move in this gap.   The activation energy is usually calculated by means of an equation analogous to the Arrhenius equation

$$p = p_0 e^{-E/RT} \tag{1}$$

where p is the resistance to separation of the splice; p_0 is a constant; E is the activation energy of the process; R is the gas constant; T is the absolute temperature.   According to this equation, a straight line should be obtained by plotting the logarithm of the resistance to separation along the ordinate axis, and the reciprocal of the absolute temperature along the abscissa axis.   Figure 3 shows such graphs for all the polyisobutylenes studied.   It is seen that all the experimental points lie fairly well on straight lines.   It is interesting that all the lines are practically parallel and that the corresponding value of the activation energy, independently of the molecular weight of the polymer, is 2390 cal.   Evidently the activation energy is the same in all cases, because the kinetic entities which participate in the diffusion process are of the same nature.   The question arises as to how can the same value of activation energy for the autohesion of polyisobutylenes of different molecular weight be reconciled with the increase in the diffusion rate which is observed with decreasing degree of polymerization.   It appears that the explanation lies in the fact that the ends of the molecules, which are more numerous in low molecular polyisobutylenes, diffuse

TABLE I

CHARACTERISTICS OF THE POLYBUTADIENES

Polymer	Content (in %) of the structural units in the main chain		Molecular weight
	1,4-	1,2-	
A	30	57	101,000
B	65	31.5	72,000

more rapidly into the polymer layer than do the middle portions of the molecules. This is quite understandable, as the probability of entry of the ends of a molecule into the gap between the molecules of the layer into which the diffusion takes place must definitely be greater, for steric reasons, than the probability of entry of a middle portion of a molecule into the same gap. It must then be assumed that the different autohesion of polyisobutylenes of different degrees of polymerization is due to differences in the value of the pre-exponential term in Equation (1), which, when the Arrhenius equation is applied to diffusion, represents the probability of entry of a molecule into a pore.

Effect of shape of the polymer molecule on autohesion.—Two butadiene polymers, A and B, were taken, with different contents of 1,4- and 1,2-structures, which were studied in detail by Tolstukhina[4]. Table I shows the contents of the 1,4- and 1,2-structural units in the polymers, determined by Prilezhaev's method and the ozonization method, and the mean molecular weights of the polymers, determined osmometrically.

It is very significant that it was established by a study of the plastic flow of polymers A and B in the solid state that the coefficient of true viscosity of butadiene polymers decreases with increase of the content of 1,4-structural units in the molecule. However, Tolstukhina's study of the rate of stress relaxation in butadiene polymers showed that the relaxation processes were more rapid for polymer A than for polymer B. Apparently the presence of a large number of vinyl side chains in the high polymer molecule weakens the interaction between the main chains.

For the determination of autohesion of butadiene polymers, they were dissolved in benzene and applied to the fabric from solution. It should be noted that polymer B did not dissolve completely in benzene, and to obtain a smooth polymer surface on the fabric strips it was necessary to separate off by filtration a small amount of a gel fraction. The same method was used by Tolstukhina in the preparation of solutions of this polymer. The fabric strips were doubled in the usual manner, with a contact time of 5 minutes and at temperatures of 20 and 60°. The separation of the splices was carried out in the usual way. The results are shown in Table II.

TABLE II

RESISTANCE TO SEPARATION AND WORK OF AUTOHESION OF POLYBUTADIENES WITH DIFFERENT CONTENTS OF 1,4- AND 1,2-STRUCTURAL UNITS IN THE MAIN CHAIN

Polymer	Resistance and work	Contact temperature in°	
		20	60
A	p (g./cm.)	34	284
	Au (erg/cm.$^2 \cdot 10^{-3}$)	66	560
B	p (g./cm.)	54	123
	Au (erg/cm.$^2 \cdot 10^{-3}$)	106	241

It is seen from the results of experiments in which doubling took place at 20° that large numbers of double bonds in the main valency chain correspond to high values of resistance to separation and work of autohesion for a given contact time.   These results confirm our previous view[1] that the presence of side chains in polymer molecules should hinder the diffusion of molecules or portions of them from one volume of the polymer into another.   When the contact temperature is raised to 60°, the position is reversed..   The cause of this is still not clear.   It is possible that in the case of the polymer with a high content of 1,2- structure, in which, as we have seen, the interaction between the main chains is less, when the temperature increases the whole molecules begin to diffuse, and not segments of them.

Effect of the number of polar groups in the high polymer molecule on autohesion. —These experiments were carried out with butadiene copolymers which contained different amounts of acrylonitrile.   Polymers with contents of 11.7;
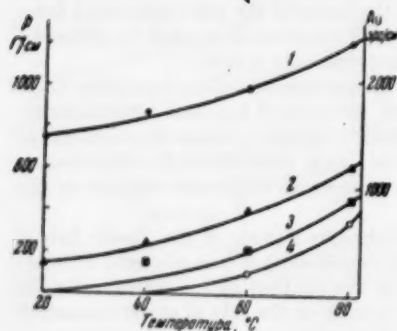
FIG. 4.—Effect of contact temperature on resistance to separation *p* and work of autohesion *Au* for butadiene-nitrile copolymers containing different amounts of acrylonitrile in the molecule: *1.* 11.7%. *2.* 19.6%. *3.* 28%. *4.* 36.9%.
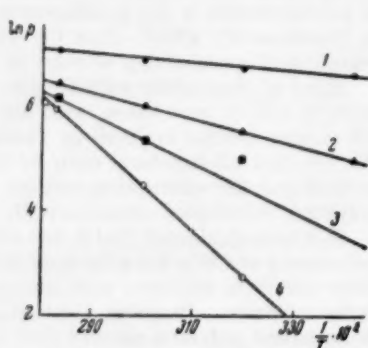
FIG. 5.—Dependence of ln *p* on 1/T for butadiene-nitrile copolymers containing different amounts of acrylonitrile in the molecule: *1.* 11.7%. *2.* 19.6%. *3.* 28%. *4.* 36.9%.

19.6; 28.0; and 36.9% of acrylonitrile were used.   The butadiene-nitrile copolymers were applied to the fabric strips from dichlorethane solution.   The contact time of the coated strips during laminating was 5 minutes.

Figure 4 presents data on the resistance to separation and work of autohesion for various butadiene-nitrile copolymers at different laminating temperatures.   As in the case of the polyisobutylenes, the curves are exponential in character.   It is interesting to note that with higher contents of polar groups in the copolymer the resistance to separation at normal temperatures is less, but the slope of the curve with increase of temperature is steeper.   This is evidently to be explained by the fact that the polar groups, as the result of formation of bonds between them, strongly hinder thermal agitation at low temperatures. As the temperature rises and thermal movement increases, the polar bonds are destroyed and the diffusion capacity increases sharply.

Figure 5 shows graphs for ln *p* against 1/T for the polymers studied.   On the whole the experimental points lie fairly well on straight lines.   It is interesting that the slope of the curve is greater with higher contents of polar groups in the copolymer.   The activation energies calculated from these graphs were as follows:

Content of acrylonitrile in the copolymer, %, 11.7, 19.6, 28.0, 36.9
Value of E in kcal, 1.53, 4.76, 8.67, 16.59

Our explanation for the increase of activation energy with increased content
of acrylonitrile in the copolymer is that as the polarity of the polymer increases,
so there is an increase in the energy needed for a segment of the molecule to
penetrate into the space between the molecules of the polymer into which the
former molecule is diffusing.

Effect of formation of spatial structures in the polymer on its autohesion.—
In this series of experiments we studied the effect of crosslinking of natural
rubber molecules by sulfur bridges in vulcanization, on autohesion.   In these
experiments the fabric strips were coated with benzene solutions of smoked
sheet, to which 5% sulfur, 1% thiuram, and 2% zinc oxide on the weight of the
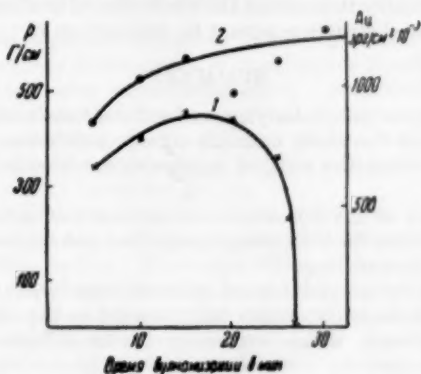
Fig. 6.—Effect of vulcanisation on resistance to separation p and work of autohesion Au of natural rubber:
1. With sulfur, thiuram, and zinc oxide. *2*. Without additions.

rubber had been previously added on the mill.   Before laminating, the strips
were heated at 100° for various periods, which resulted in different degrees of
vulcanization of the rubber strips.   Otherwise the preparation and separation
of the joints was as usual.   In addition to these experiments, a special control
series of experiments was performed, which differed only in the fact that sulfur,
thiuram, and zinc oxide were not added to the rubber.   The results of the
experiments are shown in Figure 6.

It is seen that as the vulcanization time increases the autohesion at first
increases somewhat, and then decreases sharply.   The increase of autohesion
at the start of vulcanization is explained by the fact that heating favors the
destruction of intermolecular bonds in the polymer.   Another possible explana-
tion of the increase of autohesion is that it is caused by the oxidative degrada-
tion of rubber which takes place during the process.   Decrease of molecular
size, as was seen in the case of polyisobutylene, may favor autohesion of the
high polymer.   During this time the partial formation of bridges between the
individual molecules does not yet appreciably affect autohesion.

The sharp decrease of autohesion when the time of heating is increased to
25 minutes is apparently due to the fact that then sulfur bonds already begin to
be formed between the separate aggregates formed during the first stage of vul-
canization.   A sort of jump occurs, in which the polymer containing large

numbers of sulfur bonds between individual linear molecules undergoes a transition into a qualitatively new state—a three-dimensional structure. It is clear that the formation of a spatial structure, as was shown earlier[1], should lead to complete disappearance of autohesion in the polymer.

In the control experiments the autohesion increases continuously with increasing time of thermal treatment, tending to a definite limit. The fact that the value of the autohesion in the control series is always higher is explained by the impossibility of formation of sulfur bridges.

Finally it should be noted that the curve for changes of autohesion with increase of heating time of the polymer to which sulfur and accelerators had been added may serve to characterize structural changes in the polymer during vulcanization. In this respect it presents considerable advantages, for example, over the curve which characterizes the addition of sulfur. This latter, as is known[5] changes steadily throughout the whole time of heating and the instant of formation of a spatial structure cannot be detected on it.

SUMMARY

1. It is shown for polyisobutylenes of different molecular weight that increase in the size of the chain molecule retards autohesion, but increases the limiting value to which the work of autohesion tends with increasing contact time.

2. Investigation of the temperature dependence of autohesion of polyisobutylenes showed that the activation energy does not depend on the molecular weight of the polyisobutylene.

3. It is shown for polybutadienes with varying contents of 1,4- and 1,2-structures that autohesion decreases with increase in the number of short side groups in the molecule, which apparently hinder diffusion by purely steric causes.

4. Investigation of the temperature dependence of autohesion of butadiene-nitrile copolymers with different contents of acrylonitrile in the molecule showed that the activation energy of autohesion increases with increase of polar nitrile groups in the polymer.

5. It is shown for the vulcanization of natural rubber that the formation of a spatial structure results in complete disappearance of autohesion in high polymers. It is shown that the kinetics of changes of autohesion during vulcanization can effectively characterize the structural changes which take place in the polymer during the process.

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THEORETICAL MODEL FOR THE ELASTIC BEHAVIOR OF FILLER-REINFORCED VULCANIZED RUBBERS *

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INTRODUCTION

One of the more important advances in rubber science during the past twenty years has been the development of quantitative theories describing the elastic properties of pure-gum vulcanized rubbers. As a result it is now possible to account for their equilibrium stress-strain behavior with considerable success. There is, however, no adequate theory to describe the elastic properties of filler-reinforced rubber vulcanizates and the work described herein is an attempt to provide a basis for such a theory.

When a reinforcing filler is added to rubber it produces a large increase in the stiffness of the vulcanizate. This increase is reduced and may be substantially destroyed by deformation. Numerous attempts have been made to describe the increase of stiffness resulting from the introduction of fillers and relationships describing the dependence of the modulus on the concentration and particle shape of the filler have been developed[1]. However, these do not take into account the softening which results from previous deformation and thus have limited applicability. Recently Blanchard and Parkinson[2] have attempted to develop empirical relationships to describe the elastic properties in simple extension of reinforced rubber vulcanizates after they have been previously deformed. They started with the appropriate stress-strain relationships from the classical kinetic theory and introduced two curve-fitting parameters to describe stress-strain data obtained in conventional tensile tests on a Goodbrand machine. In this way they were able to fit the course of the stress-strain data obtained after previous extension at extensions less than those previously applied and to describe the dependence of the parameters on previous deformation. Unfortunately, the significance of the parameters is obscure.

Figure 1 shows typical stress-strain curves determined in simple extension on a natural rubber tire-tread type of vulcanizate. Curve *1* is an initial stress-strain curve determined without any previous deformation of the test specimen; Curve *2* is a stress-strain curve determined after previous extension. The figure shows clearly the following features which are exhibited by filler-reinforced vulcanizates and which must be accounted for by any theory attempting to represent their elastic behavior:

(i) After previous extension the vulcanizate is markedly softer at extensions less than the maximum previously applied.

(ii) Previous extension has little influence on the stress-strain properties at greater extensions (Region *c* in Figure 1).

(iii) At extensions in the neighborhood of the maximum previous extension the stress-strain curve shows a pronounced and rapid upturn (Region *b* in Figure 1).

(iv) After previous extension the stress-strain curve shows the characteristic shape normally associated with gum vulcanizates (Regions *a* and *b* in Figure 1). The upturn (Region *b*), however, is more rapid than that of a pure gum vulcanizate and occurs at lower extensions.

Attention was drawn to the first three of these features in an earlier publication by one of the authors[3] and it has now been possible to devise a simple theory
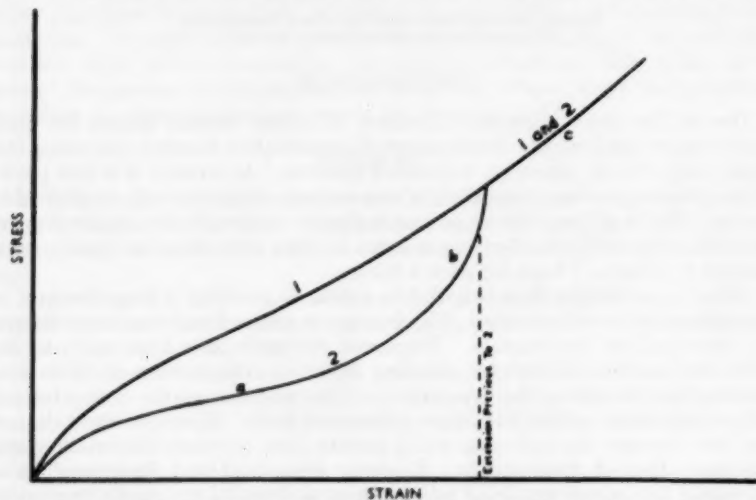
FIG. 1.—Stress-strain curves without and with previous extension.

of reinforced rubber vulcanizates in terms of a model which exhibits all of these features and enables the whole course of stress-strain curves determined both before and after previous deformation to be quantitatively described.

THEORETICAL MODEL

A filler-reinforced vulcanizate is considered to be a simple two-phase system and composed of regions of hard and soft rubber. On the application of stress most of the deformation takes place in the soft regions. The hard regions make little contribution to the deformation but they may be broken down to form soft regions by the application of stresses in excess of those previously applied. The fraction of rubber in the soft state thus depends upon the maximum stress to which the rubber has been subjected. Once softening starts at any point there is a natural tendency for it to continue across the strip of rubber, due to the resulting decrease in area of the hard rubber now supporting the applied force. Thus, it is to be expected that, after stretching, the rubber vulcanizate will be broken up into hard and soft regions in series with each other.

A simple model representing the behavior of such a material is shown in Figure 2. Here each of the two phases has been grouped, for convenience, into a single region which is in series with the other.

If a reinforced rubber vulcanizate represented by the model in Figure 2 is deformed in simple extension, then the elongation can be split up into two portions which are due to the deformation of the soft and hard regions respectively. If a fraction σ of the vulcanizate is in the soft region then the measured strain ϵ of the rubber sample is related to the actual strains ϵ_S and ϵ_H, which exist in the soft and hard regions respectively, by the equation

$$\epsilon = \sigma\epsilon_S + (1 - \sigma)\epsilon_H \tag{1}$$

It will be seen from (1) that if the contribution of the hard region to the deformation is so small that it can be neglected then the measured strain at a given stress is proportional to the fraction σ of rubber in the softened state.
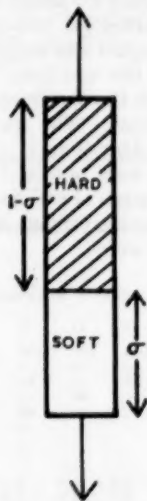
FIG. 2.—Model of reinforced vulcanizate.

It is shown in a subsequent section that in filler reinforced vulcanizates, after a given previous extension, the fraction σ is constant during subsequent stress-strain measurements before the rapid upturn, which occurs in the neighborhood of the maximum extension previously applied. One consequence of this is that, when the contribution of the hard region is neglected, stress-strain measurements determined on samples of a reinforced rubber vulcanizate, after a variety of previous extensions, should differ only in the value of σ. They should thus be capable of superposition by simply multiplying the measured value of the strain by $1/\sigma$. The resulting stress-strain curve would then be the true stress-strain curve of the material in the soft regions.

EXPERIMENTAL METHOD

Stress-strain measurements were carried out in simple extension at 25° C on parallel-sided strips of rubber about 3 mm. wide and 1 mm. thick. The strips were cut from flat sheets on the surface of which two raised parallel lines, 1 inch apart, had been molded to provide reference marks. Light clamps were at-

tached to the ends of the specimen, which was then supported from the upper one while stresses were applied by hanging weights from the lower. The distance between the reference marks was measured with a cathetometer three minutes after each increment of load, and the corresponding strain determined. The continuous creep which occurs in filler-loaded vulcanizates after the application of a load made it necessary to select arbitrarily the period which was allowed to elapse before measurements were taken. Preliminary experiments had shown that the rapid change in length, which occurs for some period after the application of load, had substantially ceased after the first three minutes and that reproducible data could then readily be obtained. For example, in a natural rubber tire tread type of vulcanizate the increase in extension between the third and tenth minutes was less than 2 per cent of the extension.

All stress-strain measurements were taken in the load-increasing direction. Stress-strain curves were determined for each specimen after various previous elongations. The procedure adopted was as follows: measurements were made during the initial extension of the specimen to a chosen (low) elongation; measurements were then made on the specimen during successive extensions to progressively increasing elongations. The specimen was allowed to relax for ½ hour at zero load before each extension.

Series of stress-strain curves were obtained in this way for natural rubber vulcanizates containing various types of carbon black and other fillers and for a GR-S tire tread type vulcanizate containing MPC black. Compounding details and vulcanizing procedures were:

Sulfur 3, zinc oxide 5, antioxidant 1, with:

	A	B	C	D	E	F	G	H	I	J	K
Natural rubber	100	100	100	100	100	100	100	100	100	100	—
GR-S	—	—	—	—	—	—	—	—	—	—	100
MPC Black	50	30	20	—	—	—	—	—	—	—	50
EPC Black	—	—	←	50	—	—	—	—	—	—	—
HAF Black	—	—	—	—	40	—	—	—	—	—	—
FT Black	—	—	—	—	—	40	—	—	—	—	—
Magnesium carbonate	—	—	—	—	—	—	40	—	—	—	—
Calcium silicate	—	—	—	—	—	—	—	40	—	—	—
Whiting	—	—	—	—	—	—	—	—	40	—	—
Stearic acid	3.0	2.2	1.8	3.0	3.0	3.0	3.0	3.0	3.0	1.0	2.0
Mercaptobenzothiazole	1.0	0.8	0.7	1.0	1.0	1.0	1.0	1.0	1.0	0.5	—
N-Cyclohexylbenzothiazole-2-sulfenamide											1.0
Process oil											6
Vulc., mins. at 140° C	60	45	45	60	40	40	40	40	40	45	60

RESULTS

Figures 3 and 4 show typical families of stress-strain curves obtained on a natural rubber (Mix A) and a GR-S (Mix K) tire-tread type of vulcanizate containing MPC black. The figures show stress-strain curves obtained on samples without previous elongation and after selected previous elongations. For the sake of clarity experimental points determined at low extensions have been omitted from some of the curves. There was appreciable permanent set present at the commencement of stress-strain curves determined after the larger elongations. To make allowance for this, the set present was subtracted from all measurements of length between the reference lines made during the course of the stress-strain curve. The strains and stresses were then calculated relative to the original dimensions of the test specimen. As a result all of the stress-strain curves pass through the origin.

The figures clearly show the characteristic features of reinforced vulcanizates which have been previously stretched.
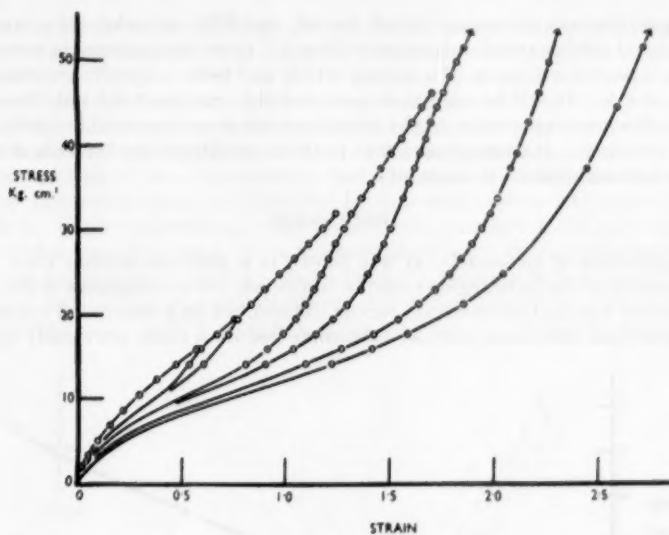
Fig. 3.—Stress-strain curves on natural rubber tread vulcanizate.
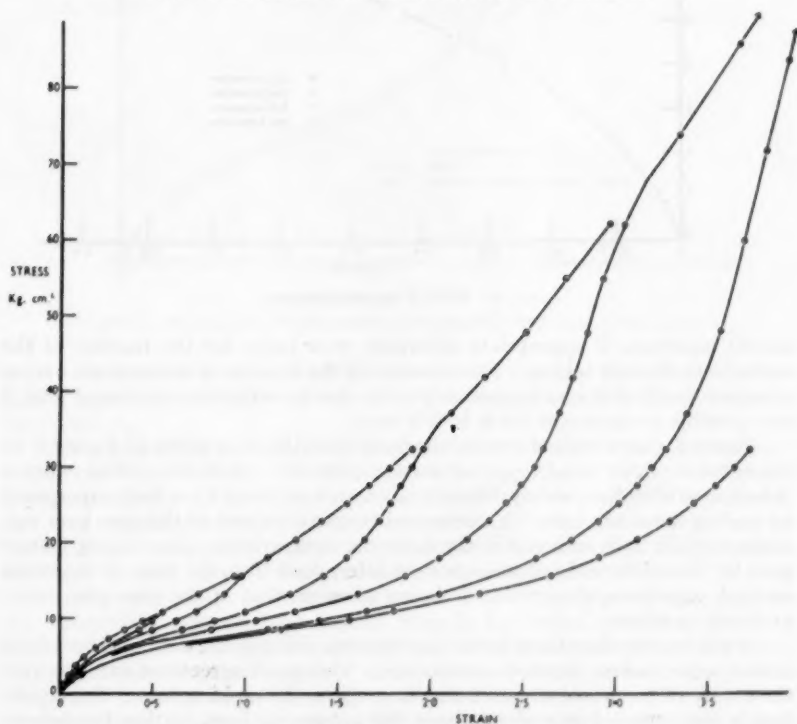
Fig. 4.—Stress-strain curves on GR-S tread vulcanizate.

Figure 5 shows the second, third, fourth, and fifth extensions of a sample of
the natural rubber tread vulcanizate (Mix A); these measurements were made
during repeated extension of a sample which had been originally extended to a
strain of 1.5. It will be seen that provided the extension did not closely ap-
proach the maximum value of the initial extension no appreciable further soft-
ening occurred.   It thus appears that in these conditions the fraction of rubber
in the softened state σ is constant.

DISCUSSION

Application of the model.—It was shown in a previous section that, if the
deformation of the hard region could be neglected, one consequence of the model
introduced was that stress-strain curves, determined on a reinforced vulcanizate
after previous extensions, and at extensions less than those previously applied,
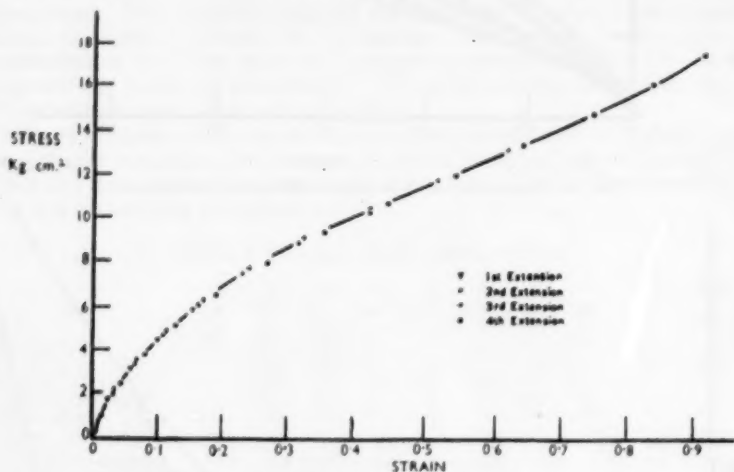
FIG. 5.—Effect of repeated extension.

should superpose if appropriate allowance were made for the fraction of the
rubber σ in the soft region.   Examination of the families of stress-strain curves
obtained on all of the vulcanizates used in this investigation confirmed that it
was possible to superpose them in this way.

Figure 6 shows typical results obtained from the data given in Figure 3 on
the natural rubber tread type vulcanizate (Mix A).   Here stress-strain curves
determined after four widely different previous extensions have been superposed
by scaling the strain axis.   A stress-strain curve obtained on the pure gum vul-
canizate (Mix J) is included in the figure for comparison.   The scaling factors
used for the reinforced vulcanizate were determined from the ratio of the strain
on each experimental curve at a chosen stress to that of the pure gum curve
at the same stress.

It will be seen that there is excellent superposition of the data obtained from
curves after various previous extensions.   This good agreement extends over
the course of the whole stress-strain curve up to the rapid upturn.   Superposi-
tion is not expected in regions above the upturn, as here, further breakdown

occurs during the extension and the fraction of rubber in the softened state changes by varying extents.   Nevertheless, the curves are still not grossly different.

Comparison of the stress-strain curves obtained on the reinforced vulcanizate with that obtained on the pure gum vulcanizate shows clearly the similarity in the shape of the stress-strain curves.   This similarity is apparent at all extensions, and all of the characteristic features of stress-strain curves obtained on pure gum vulcanizates are exhibited by previously extended reinforced vulcanizates.   It thus appears that the stress-strain behavior of the soft region in the model is closely similar to that exhibited by pure gum vulcanizates.   It should be emphasized here that close agreement between the stress-strain behavior of the pure gum vulcanizate and the scaled results on the reinforced vulcanizate should not be expected.   The pure gum vulcanizate was chosen
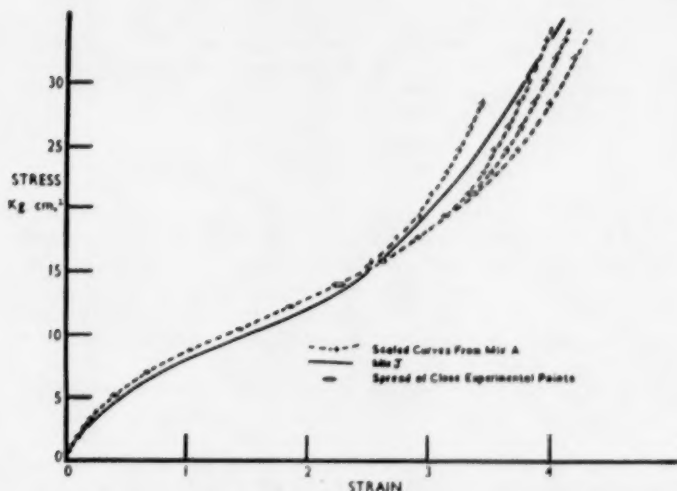
FIG. 6.—Superposition of stress-strain curves after different previous extensions.

somewhat arbitrarily and a small difference in the degree of vulcanization could easily result in much closer agreement.   This feature will be discussed in more detail below.

The results reported indicate that the stress-strain properties, in simple extension, of filler reinforced vulcanizates can be described in terms of the model advanced above.   The rubber vulcanizate is assumed to consist of two phases, one hard and the other soft, the hard region being converted to the soft one by the application of sufficient stress.   During the initial extension the fraction of rubber in the soft region increases continuously with increase of stress.   During subsequent extensions, at stresses less than the maximum previously applied, the vulcanizate deforms more readily than in the initial extension, due to a larger fraction of rubber in the soft region.   The fraction of rubber in the soft region remains constant until the stress approaches the previous maximum. Thereafter it increases continuously as in the initial extension.

Stress-strain curves determined after previous extension show a rapid upturn

in the neighborhood of the maximum previously applied.   This upturn is associated with the pronounced stiffening which occurs in pure gum vulcanizates at high extensions, and which results from either or both (i) the finite extensibility of the long chain rubber molecules or (ii) crystallization produced by extension.   Although the upturn may appear at low overall extensions of the reinforced vulcanizate this is due to there being only a small fraction of the rubber in the soft region, the actual extension of rubber then being high. Figures 3, 4, and 6 show that the upturn occurs at the same stress irrespective of previous extension and further confirm this view.

Quantitative interpretation of results.—The development of this analysis on a quantitative basis demands a knowledge of: (i) the stress-strain properties of the soft region; (ii) the dependence of the fraction of rubber in the soft region on extension or applied stress; and (iii) the stress-strain properties of the hard region.

Consider firstly the stress-strain properties of the soft region.   It was shown earlier that they closely resemble those of pure gum vulcanizates.   A well established theory for the behavior of pure gum vulcanizates already exists, and their stress-strain behavior at low and moderate extension has been shown by Rivlin and Saunders[4] to be described by the relation

$$f = 2A_0(\lambda - 1/\lambda^2)(C_1 + C_2/\lambda) \tag{2}$$

where f is the force, A_0 the original cross-sectional area, λ the extension ratio, and C_1 and C_2 constants characterizing the rubber.   At relatively high extensions, where either or both the finite extensibility of the long chain rubber molecules and crystallization resulting from extension influence the stress-strain behavior, this relation is no longer applicable.   It has been found that C_1 is a function of the degree of vulcanization and C_2 is a constant, describing departures from the simple kinetic theory[5].

In each case, examination of the stress-strain curve obtained after superposition showed that it could be closely fitted by curves given by Equation (2); the values of C_1 and C_2 being adjusted to give the best fit.   It will be recognized that, in fitting Equation (2) to these stress-strain curves, the values of C_1 and C_2 are strongly influenced by the values of σ (the fraction of rubber in the soft region).

In Equation (2)

$$\lambda = \frac{\lambda_M - 1}{\sigma} + 1 \tag{3}$$

where λ_M is the overall extension ratio and λ refers to the soft region alone.   As a result there are three adjustable parameters C_1, C_2, and σ.   The procedure adopted was to find the values of C_1 and C_2 for a theoretical curve (given by Equation (2)) which gave, over the whole stress-strain curve, a constant value for the scaling factor relating the curve obtained from each of the reinforced vulcanizates after superposition and the theoretical curve.   It was found that small differences in C_1 and C_2 resulted in substantial variation in the scaling factors over the course of any one stress-strain curve and that the values of C_1 and C_2 could be determined precisely.

Figure 7 shows the data previously given in Figure 6 of the superposition of stress-strain curves determined on the natural rubber tire tread mix after four widely different previous extensions but in this figure they have been scaled to
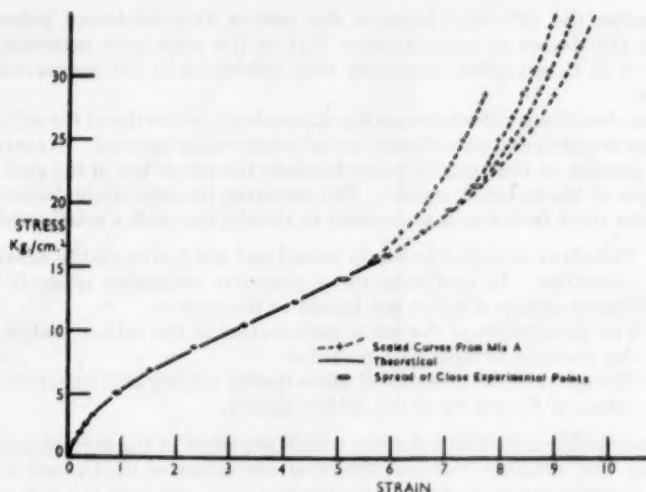
FIG. 7.—Superposition of stress-strain curves after different previous extensions.

fit a theoretical curve given by Equation (2). It will be seen that the theoretical curve with values of both C_1 and C_2 of 1.0 kg./cm.^{2} gives an excellent fit to the experimental results over the whole range where the theoretical relation is applicable. This agreement is typical of that obtained with all of the vulcanizates used and it thus appears that the stress-strain properties of the soft regions of the model for reinforced vulcanizates can be described by existing high-elasticity theory over the range of extensions before the rapid upturn.

The values of C_1 and C_2 determined for the soft regions of all the natural rubber vulcanizates used are given in Table I.

It was mentioned earlier that in pure gum vulcanizates the value of C_1 was proportional to the degree of crosslinking, and that the value of C_2 was a constant independent of the degree of crosslinking. For accelerated sulfur pure gum vulcanizates it has been found previously that the value of C_2 is 1.0 kg./sq. cm.^{5} This value is the same as those given in the last column of the table for the soft regions of all of the filler reinforced natural rubber vulcanizates. It thus appears that the stress-strain curves of the soft regions of all of these vulcanizates can be closely fitted by stress-strain curves obtained on pure gum

TABLE I

Natural rubber filler	C_1 kg./cm.^{2}	C_2 kg./cm.^{2}
Mix A MPC Black (50 parts)	1.6	1.0
Mix B MPC Black (30 parts)	1.1	1.0
Mix C MPC Black (20 parts)	1.0	1.0
Mix D EPC Black (50 parts)	0.9	1.0
Mix E HAF Black (40 parts)	1.3	1.0
Mix F FT Black (40 parts)	1.5	1.0
Mix G Magnesium carbonate (40 parts)	1.0	1.0
Mix H Calcium silicate (40 parts)	0.65	1.0
Mix I Whiting (40 parts)	1.2	1.0
Mix J Pure gum	1.2	1.0

vulcanizates, the difference between the various filler reinforced vulcanizates being in the degree of vulcanization (C_1) of the pure gum materials. The differences in C_1 are quite consistent with differences in the compounding ingredients.

These close similarities between the stress-strain properties of the soft regions and those of pure gum vulcanizates are of considerable interest. Nevertheless, it is not possible at this stage actually to relate the properties of the gum matrix with those of the softened region. The following imperfectly understood considerations must be taken into account in developing such a relationship:

(i) The effect of rigid fillers both bound and not bound on the stress-strain properties. In particular the appropriate correction to apply for the diluent action of fillers not bound to the rubber.

(ii) The disturbance of the affine deformation of the rubber matrix due to the presence of rigid filler particles.

(iii) The effect of the presence of fillers during milling and vulcanizing upon values of C_1 and C_2 of the rubber matrix.

These considerations do not come within the scope of the present paper, but they may well influence the final choice of the values of C_1, C_2, and σ.

The absolute determination of the fraction σ of rubber in the soft region is necessarily part of the above determination of the stress-strain properties of the soft region. However, relative values of σ, after various previous extensions, can be determined simply from the scaling factor to produce superposition. These relative values of σ involve no assumption about the stress-strain properties of the soft region.

The change in the value of σ with previous extension was determined for all of the natural rubber vulcanizates. It was found that curves of σ against previous strain ϵ_P always gave a positive intercept at zero strain. This can be interpreted either as a small degree of breakdown existing before the initial extension, or in terms of the hard region having a finite modulus and making an appreciable contribution to the measured strain.

If it is assumed that the reinforced vulcanizates are homogeneous before the initial extension then the second of these possible explanations applies. The value of the fraction σ then becomes

$$\sigma = \frac{\sigma' - \sigma_0'}{1 - \sigma_0'} \tag{4}$$

where σ_0' is the value obtained when it is assumed that the hard region is inextensible. The relationship given in Equation (4) is determined from the assumption that the ratio of the strains in the hard and soft regions is constant and equals σ_0' and that the strain in the soft region is not modified by the correction. This allowance for the contribution of the hard region to the extension does not therefore affect previous conclusions about superposition of the stress-strain curves after previous extension or of the values of C_1 and C_2 characterizing the behavior of the soft region.

Thus, in this quantitative description of the stress-strain properties of filler reinforced vulcanizates there is a choice of two procedures. In the first of these it is assumed that the hard region is inextensible; in the second the hard region is considered to make its own contribution to the deformation. Whichever procedure is selected, simple selfconsistent methods for describing the stress-strain properties have been developed. The differences between the two meth-
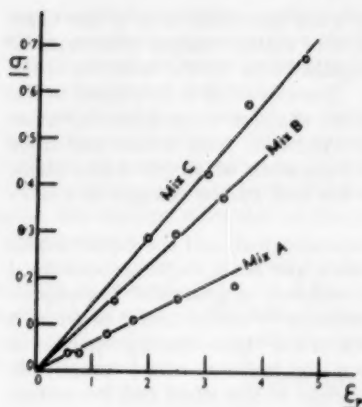
FIG. 8.—Change of σ with extension. Effect of concentration of carbon black. Mix A, 50 pts.; Mix B, 30 pts.; Mix C, 20 pts.; MPC black.
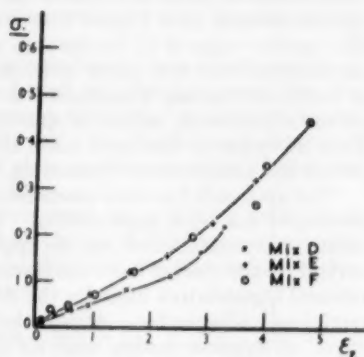
FIG. 9.—Change of σ with extension. Effect of type of carbon black. Mix D, EPC; Mix E, HAF; Mix F, FT black.

ods are not considered to be of great importance as the contribution of the hard region to the deformation is relatively small.

The change in the values of σ with previous extension ϵ_P for the different vulcanizates are shown in Figures 8, 9, and 10. In these figures the value of σ has been corrected for the finite modulus of the hard regions, and in consequence, at zero extension, the value of σ is always zero.
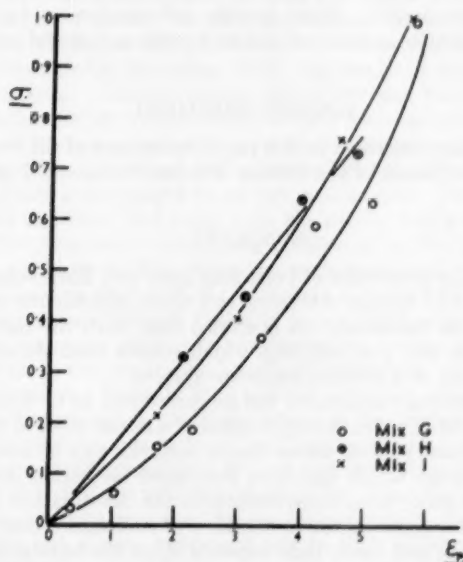
FIG. 10.—Change of σ with extension. Various white fillers. Mix G, magnesium carbonate; Mix H, calcium silicate; Mix I, whiting.

General.—A natural consequence of the work described here is the characterization of fillers in terms of (*a*) the value of σ after various extensions or applied stresses, as in Figures 8, 9, and 10, together with (*b*) the influence of the filler on the value of C_1 for the soft region.   However, this is incidental to the main objective of this paper which is to put the complex stress-strain behavior of reinforced rubber vulcanizates in simple extension, both before and after previous extension, within a quantitative framework of simple basic ideas. Thus no endeavor has been made to follow the well known changes in σ with period and temperature of standing.

The approach has been essentially phenomenological, and the simple model developed has wide applicability.   Its features are not specific to reinforced rubber vulcanizates and can be applied to materials in general.   The experimental results quoted have convincingly confirmed its utility and it provides a rational quantitative basis for the description of the stress-strain properties of reinforced vulcanizates.   Application of the model to the so-called "amplitude effect" in dynamic testing confirms the parallelism of this effect and the softening produced by simple extension of reinforced vulcanizates.

Apart from the very good portrayal of experimental data, a great advantage of the simple model is that the physical picture involved appears highly probable.   Indeed, visible evidence of the coexistence of hard and soft regions in rubber vulcanizates and the transfer of rubber from one region to the other during stretching can readily be found.   Examples occur during the stretching of vulcanizates containing relatively large concentrations of poorly reinforcing filler, and of vulcanizates stiffened by crystallization as a result of exposure to low temperatures.

Speculation as to the interpretation of the results in terms of rubber-filler interaction and the nature of reinforcement is considered to be both inappropriate and undesirable.   More specific information as to the nature of rubber-filler interaction is required before precise and useful comment can be formulated.

ACKNOWLEDGMENT

SUMMARY

The stress-strain properties of both pure gum and filled vulcanized rubbers have been studied in simple extension and their dependence on previous deformation has been examined.   It is shown that both the increased stiffness produced by fillers and the softening which results from deformation can be interpreted in terms of a simple two-phase system.

The filler-reinforced vulcanizate can be considered to be composed of zones of hard and soft rubber.   On the application of a stress, most of the deformation takes place in the soft regions whose elastic behavior can be described in terms of the classical theory which has been developed for highly elastic materials. The hard regions make little contribution to the deformation but are broken down to form soft regions by the application of sufficient stress.   The fraction of the rubber in the soft state thus depends upon the maximum stress previously applied.

The stress-strain behavior of the composite material can be represented

most simply by a model in which the hard and soft regions are in series, and in which, to a first approximation, the hard regions are assumed to be inextensible. The observed deformation at any stress is proportional to the fraction of the rubber in the softened state.

Analysis of the stress-strain curves of filler-reinforced vulcanizates measured both before and after previous deformation has shown that it is possible to describe their course in terms of (1) a stored energy function given by high elastic theory and appropriate to the rubber matrix; and (2) a single parameter which gives the fraction of rubber in the softened state and is a function of previous deformation.

In particular, each stress-strain curve obtained on any filler vulcanizate system at elongations less than the previous maximum elongation can be superimposed on that of the rubber matrix by multiplying the strains by the appropriate factor given by the parameter above.

CONFERENCE DISCUSSION

Mr. BRYANT considered that the authors had made a very valuable point which had been neglected in the past, namely that if with filled materials one was going to apply an equation similar to the equation for unfilled rubber, then one must apply it to the equilibrium state and not simply to the first elongation. Following from that he wished to take issue with the authors on the adequacy of their picture of what was happening in a filled rubber which had been stretched.   On the basis of his own work, it had been felt that in a filled rubber which had been stretched one had something which bore a resemblance to a foamed rubber.   One had a spongelike material in which the filler was stuck to the rubber in some parts but in other parts it had come unstuck and the filler particles were simply resting in the holes, with the vacuoles round them, when the specimen was under stress.   It therefore seemed unwise to try and relate the properties of a filled material in which the rubber was partially at least in a spongelike condition to the equation which one obtained from considering a solid block of material.   One of his own colleagues had had some success in deriving an equation for the stress-strain curve of a sponge material, and probably a synthesis of that approach with the authors' model would lead to a more accurate physical picture of what was going on, though there did seem to be one or two difficulties which might be all but insuperable.   For example, when the filler particles had been torn away from the rubber and were resting in the holes of the rubber, they were introducing constraints on the movement of the rubber and one would be getting stress concentrations, and while he was not for one moment denying the value of the present approach to that problem, it might be very much more difficult than the paper might suggest.

Mr. MULLINS, in reply, wished to emphasize one or two points which had been made in detail in the paper, and principally that their conception was one of soft and hard regions.   Initially they had not identified the soft regions with pure gum rubber vulcanized to the same extent as the carbon black material; they had just imagined regions soft and hard and were not postulating exactly what were the stress-strain qualities of the soft regions.   Experiment had shown that with filled rubbers of the sort described in the paper the elastic properties of the soft region could be described by the high elasticity theory.   That was a subsidiary point but a very important one in their effort to describe their behavior quantitatively.

He agreed, of course, that in a filled rubber where there was poor union be-

tween filler and rubber one had to have something of the sort of a sponge, with particles rattling round like peas in the hole of the sponge, but he did not think that detracted at all from the paper.   He and his coauthor put it forward as a first approximation of the method describing the stress-strain properties. Quite clearly it may be desirable to embellish it to take care of things such as that, but they were pleased to think they could get hold of stress-strain properties of black rubbers so well.

Dr. MARSHALL, referring to Figure 1, asked how the model explained the fact that Curves 1 and 2 did not join at the same point—at the point where the vertical line representing the previous extension intercepted both of them.   In terms of strain the difference was possibly somewhat trivial, but in terms of stress it was quite substantial, and when considering the constitution of the soft and hard regions that difference might be a matter of importance.

Secondly, had the authors any observations to make on the stability of their model?   Considering Figure 2, if one applied a little more stress to the model, then some of the hard rubber would become soft, the cross-section would go down, greater stress would result, and the model would become softer.   Under some conditions—he did not know what they were—such a model would be stable; under some other conditions he imagined it would be unstable.

A general observation which he wished to make was that there were three kinds of phenomena which seemed similar.   There were the effects described by Mullins in his present paper, and also his previous work in which he had shown that the softening which resulted from prestressing rubber recovered with temperature and time.   Then again there was the phenomenon of permanent set, which also recovered with temperature and time.   Finally, there were the electrical resistance changes and these also recovered with temperature and time.   He wondered whether the authors felt that these similarities were coincidental or whether there might well be a connection between them.

Finally, the authors' model, and also various other theories of the softening due to prestressing, assumed that the energy in the first hysteresis cycle went towards overcoming a potential barrier.   It might be a very good experiment if someone could determine thermometrically how much of this energy appeared as heat.

Mr. MULLINS, replying to Dr. Marshall's first point with regard to Figures 1 and 2 and the noncorrespondence of the intersection of Curve 2 and Curve 1 with the previous extension, said the reason for that was clearly that during Curve 2 further breakdown occurred.   Measurements had been carried out to investigate this feature and it had been found that in the course of Curve 2 the region lower than the rapid upturn did not produce further breakdown, but during the course of that rapid upturn further breakdown was occurring, and that was the reason why the points did not coincide.

Referring to the stability of the model, the picture put forward by Dr. Marshall about a sort of cataclysmic process going on was possible; it did not occur with carbon black loaded rubbers or with the other rubbers which had been tested, but obviously it was possible.   He thought that the materials which Mr. Bryant was going to describe were materials of this type: the flat plateaus which he showed in his curves were characteristic of materials showing this instability, but that might well be a point which could be deferred until the following day, when Mr. Bryant presented his paper.

The next point raised by Dr. Marshall was about the connection between a variety of properties—electrical resistance, softening and permanent set.   Mr. Mullins said he would like to add a fourth one, namely plasticity or viscosity

measurements on loaded rubbers.   There clearly appeared to be some common basis.   The basic phenomenon which was occurring was the same; there would be other factors contributing differences between these properties but the basic process was the same and they were all interconnected.

Finally, Dr. Marshall's last question was associated with heat and energy and deformation, and the point made by him was a fair one.   In their present work they had been thinking in terms of stress, and had not identified the energy of deformation with the work done in breaking down the unions.   There was a critical stress at which those unions broke down.   He imagined one would observe a considerable dissipation of energy in the form of heat during the processes under consideration.

Mr. PICKETT referred to the fact that the word "reinforcement" was being used in both papers, and Mr. Bryant had, of course, mentioned the spongelike structure.   It was a great pity the various papers on reinforcement were in two different Sessions, as it seemed to be divorcing the chemical and physical aspects. It seemed that Mr. Mullins was only speaking of a physical bond whereas doubtless in the papers on the following day something would be mentioned of the chemical nature of the bond.   When one talked of a nonactive filler like whiting the spongelike conception seemed to hold good, whereas when one was dealing with carbon black the chemical nature of the bond also came into it.

Mr. MULLINS, in reply, said the word "reinforcement" occurred in his paper only as a description of the filler; in other words, he had talked about reinforcing fillers, which was common parlance in the rubber industry, but that was the only context in which he had introduced the word "reinforcement".   Consideration was only being given to stress-strain properties and hence he had avoided using that word.   He had also avoided discussing physical and chemical bonds.   Undoubtedly before the next two days there would be quite a lot of discussion about the question of chemical and physical bonds but he had deliberately avoided them in an endeavor to get away from scientific jargon to describe the qualities which were being considered.   It was possible to lose oneself in the pseudoscientific use of the terms chemical and physical bonds.

Mr. BLANCHARD said he believed that this interesting paper would provoke thought on some aspects of the behavior of rubber containing fillers, and stimulate further experimental work.   He was particularly interested by the concept of hard and soft regions in reinforced rubber as a possible explanation of the early upward sweep of the stress-strain curves of prestressed vulcanizates, i.e., reinforced rubbers in which little softening is occurring with extension.   On that point he would like to ask the authors whether they had examined the behavior of highly crosslinked gum vulcanizates comparable to the prestressed vulcanizates containing carbon black.   These would be free from any inhomogeneity introduced by reinforcing fillers.

The author had referred to the approach to the problem described by himself and Dr. Parkinson.   He suggested that any obscurity in the significance of that approach was less than in a treatment which abruptly divided the material into categories of hard and soft, with a parameter expressing the fraction of rubber in the soft region, and a model which took the hard and soft regions to be simply in series.   The pot should not call the kettle black, unless it be a frank admission of their mutual shortcomings.   The authors had put forward a simple, interesting model which could reproduce the behavior of reinforced rubber on extension: he believed they would agree in emphasizing the dangers of identifying the model too closely with reality.

Dr. WAKE said Mr. Mullins and Mr. Tobin should be congratulated on a

very elegant paper, the simplicity of which meant that even the ordinary chemist could understand something of the physics, and that was a great advantage in a gathering of rubber technologists, when many of the people, including himself, were after all only humble chemists!

He wanted to ask Mr. Mullins whether the upward sweep which showed so clearly, for example, in Figure 3, and even better perhaps in Figure 4, could be associated with the crystallization of the soft regions each time, in which case one wondered whether one could estimate the amount or the extent of the soft regions by the apparent amount of crystallinity.

Secondly, he had been looking at an earlier paper by Mr. Mullins some little while ago, and had attempted to see if he could get an energy value to associate with the structure. He had been unable to see any way of obtaining the energy of breakdown but since the structure was reformed on heating he had got some data from an earlier paper on the energy of the formation of structure, and it came out to be a very low figure—something like 2 or 2½ kilocalories per mole. That being so, with his unfortunate chemical mind, of course, he had done what Mr. Mullins had requested them not to do, and had been starting to think in terms of chemical and physical bonds.

Dr. Wake said he was wondering whether, reinforcing the previous speaker's remarks, some measurements of energetics might not usefully contribute at that stage to clarify the picture which was being presented, and which he agreed fitted the facts so remarkably well.

Mr. MULLINS, replying with regard to the upward sweep of stress-strain curves on rubbers which had been previously stretched, said the pronounced upward sweep which one saw in Figures 3 and 4 was associated with the upward sweep that one got in pure gum vulcanizates at high extensions. This was due to one of two causes: one being crystallization in natural rubber and the other the finite extensibility of the long chain molecules.

With regard to the point about the energy value, he felt that they were looking for some neatly conceived piece of experimental work to illuminate that field, and he agreed that such a study may well be rewarding. As he had said before, in a crusading spirit, one wanted to get away from the jargon of reinforcement and try to think in rather simpler terms. The field was bogged down at the moment in a morass of terms and conceptions and some cleancut experiments were necessary. He certainly agreed with Dr. Wake that measurements of energetics might be of assistance.

Referring to Dr. Wake's final comments, Mr. Mullins said he had nothing to add to the point which had been put so ably.

Dr. DE DECKER agreed that the paper presented a very useful simplification, and on examining it a little more closely it could be seen that that simplification dealt with those vulcanizates of which the modulus had been increased by adding rigid filler particles, no matter whether there were chemical, or physical, or both kinds of bonds.

Recently another class of materials had become of some technical importance, namely what might be called resin rubbers, which might be either high styrene copolymer blends or mixtures of cyclicized rubber with natural rubber, and it was known that those materials also had a pronounced increased modulus. Could some useful application be made of the new theory put forward by Mr. Mullins, in that class of materials?

Mr. MULLINS said the only comment he could add with regard to the testing or resin rubbers and the measurement of stiffness was to agree that resin rubbers

did show, as Dr. de Decker had termed it, a modulus effect, and therefore the model which had been put forward applied to those systems. He and his co-author had naturally measured the stress-strain properties of resin rubber and described them in this way.

Mr. STAFFORD asked whether Mr. Mullins considered that his simple model concept could be applied to repeated cyclic stressing; in other words, to a dynamic test. Did he see the possibility of predicting, say, the hysteresis loop?

Mr. MULLINS, in reply, said in his view the model had generality and therefore it should be capable of application to dynamic measurements. There was a brief mention in the paper that the amplitude effects which were observed in the dynamic testing of filled rubbers might well be described in this sort of way. Where structural breakdown was occurring a model of that type was a useful starting-point.

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CHANGES OF ELECTRICAL RESISTANCE OF RUBBERS LOADED WITH CARBON BLACK *

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The changes in electrical resistance accompanying the deformation of electrically-conducting natural rubber, Butyl rubber, Neoprene and Thiokol FA have been studied under static and dynamic conditions. The results have been interpreted in terms of variations in the contact resistance between adjacent particles of carbon black.

INTRODUCTION

Many workers[1,2,3,4,5] have studied the changes in resistivity that occur on deforming rubbers loaded with carbon black. This paper describes three types of experimental investigation that do not seem to have received detailed study previously, and also a theory that explains the results qualitatively in terms of variations of contact resistances between carbon black particles.

Firstly, the changes of resistance of vulcanized natural rubber, Butyl rubber, Neoprene, and Thiokol FA loaded with carbon black have been studied during cyclic deformations. Secondly, the initial increase of resistance during stretching testpieces of vulcanized natural rubber containing several loadings of different carbon blacks has been investigated. Finally, the changes of resistance with time that occur after stretching and releasing samples of electrically conducting rubber have been studied.

The ingredients and preparation of the compounds used in experiments discussed in this paper are listed in the Appendix.

The testpieces used in the following experiments were approximately 0.7 cm. wide, 0.1 cm. thick, and 7.0 cm. long. Electrical contact was established by means of brass strips bonded by molding into the ends of the samples, so that the direction of current flow was along the length of the pieces, and in the same direction as the extensions.

CYCLIC EXPERIMENTS

Testpieces of various carbon-loaded polymers have been subjected to three kinds of strain cycle.

(*a*) Successive extension and retraction performed in discrete increments with 1-minute intervals between each change of strain. A single resistance measurement was taken immediately after each change in length.

(*b*) Continuous extension at a constant speed followed by continuous relaxation at a constant speed with a time period of about 2 minutes. The resistance of the testpiece was continually recorded in terms of the deflection of a Fielden servograph.

(c) Approximately sinusoidal extension of about twenty per cent with a periodicity of about one per second. The resistance of the testpiece was recorded by observing the potential across it with a cathode ray oscillograph. A photographic record of the oscillograph trace was obtained. In this part of the experiment more reliance may be placed on the changes of resistance which were measured directly than on the absolute value obtained by normalizing with a measured mean value.

Fig. 1.—Testpiece resistance and the associated elongation E both plotted as functions of time. Results are shown for three different types of strain cycle applied to samples containing 62.5 parts of Philblack O per hundred of natural rubber.

Separate testpieces were used for each experiment except for those from which Figure 5 was plotted. The three experiments resulting in Figure 5 used one testpiece of rubber.

Figure 1 shows resistance as a function of strain for natural rubber loaded with Philblack O. Upon first stretching the resistance rises, and upon first retracting the resistance again rises. For subsequent cycles the resistance has two maxima during each cycle; one maximum occurs at minimum strain and one maximum occurs at maximum strain. Similar results were also obtained for Neoprene and Butyl rubber. Figure 2 shows results for Neoprene and Butyl rubber using one type of strain cycle.
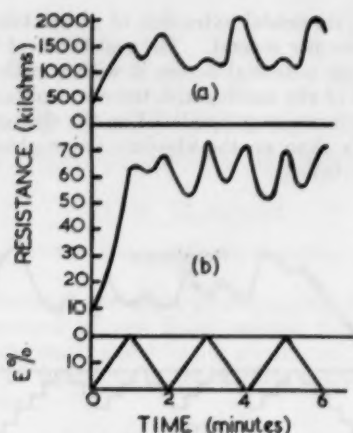
Fig. 2.—Testpiece resistance and the associated elongation E both plotted as functions of time.   Curve (a) refers to Neoprene loaded with 50 parts of Philblack O per hundred of polymer, and Curve (b) refers to similarly loaded Butyl rubber.

Figure 3 shows resistance as a function of time for Thiokol FA loaded with Philblack O.   It can be seen that this result is somewhat similar to those from the other polymers.   There is a small increase in resistance during the initial stages of the first extension, and subsequently the resistance is a maximum at maximum strain.   The absence of the second maximum may be related to the fact that the first resistance increase is small.

Figure 4 shows resistance as a function of strain for natural rubber loaded with three concentrations of Shawinigan black.   The relative prominence of the two maxima depends on black loading.

Figure 5 shows the resistance as a function of strain for the same testpiece of conducting natural rubber during three strain cycles.   The strain cycle having the highest average extension can be seen to result in the lowest average resistance.

RESISTANCE INCREASE DURING INITIAL EXTENSION

Samples of natural rubber compounds containing varying concentrations of four different kinds of carbon black were stretched to 20 per cent extension and the resistances measured.   Care was taken that the samples should not be
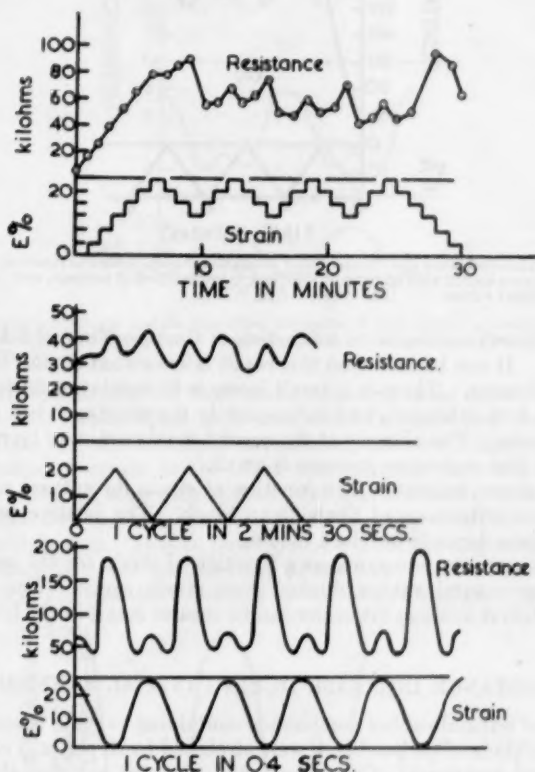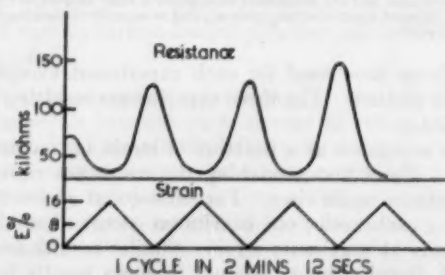

Fig. 3.—Testpiece resistance and the associated elongation E both plotted as functions of time.   Results are shown for Thiokol FA loaded with 50 parts of Philblack O per hundred of polymer.
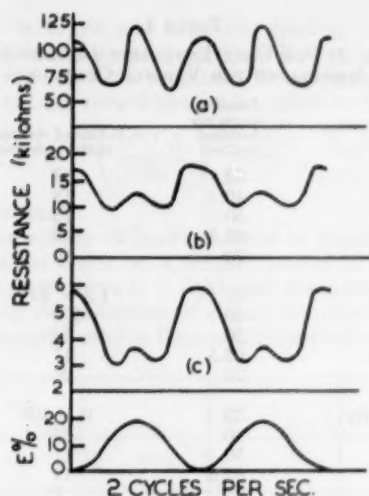
FIG. 4.—Testpiece resistance and the associated elongation E both plotted as functions of time.   The results refer to natural rubber loaded with Shawinigan black, (a) 50 parts per hundred rubber, (b) 62.5 parts, (c) 70 parts.

deformed between leaving the mold and performing these experiments.   Table I summarizes the results which were obtained.   It can be seen that for a given black the values of r (the resistance immediately after stretching divided by the initial resistance) decrease as the black concentration increases.   This result is not very surprising, since it is well known[1] that the rate of increase of resistance with reduction in black concentration is much greater at low black loadings than at high ones.   It is to be expected that stretching should reduce the number of black particles participating in the conduction process, and should thus produce larger resistance changes at low concentrations.
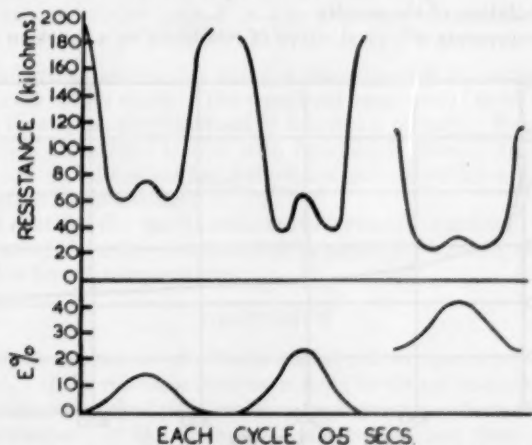
FIG. 5.—Testpiece resistance and associated elongation E both plotted as functions of time.   Single cycles are drawn from cyclic experiments at different amplitudes.   In each case the sample contained 62.5 parts of Philblack O per hundred of natural rubber.

TABLE I

RESISTANCE AT 20 PER CENT EXTENSION DIVIDED BY THE INITIAL
RESISTANCE FOR VARIOUS COMPOUNDS

Black	Loading (parts per hundred rubber)	r = Extended resistance ÷ initial resistance	$Log_{10}S$*
Spheron C	32	48	3.41
	40	18	3.17
	50	15	2.63
	62.5	12	2.17
	70	10	2.45
Philblack O	32	1.3×10^4	3.90
	40	590	3.67
	50	53	2.70
	62.5	17	1.75
	70	26	2.44
Dunlop high conductivity	32	9×10^3	4.31
	40	24	2.24
	50	11	1.79
	62.5	11	1.30
	70	7	1.39
Shawinigan	32	214	2.79
	40	128	2.74
	50	29	1.80
	62.5	12	1.34
	70	6	1.07

* S initial resistivity in ohm cm.

VARIATIONS OF RESISTANCE WITH TIME

A number of investigators[1,2,3] have studied the variations of resistance with time that occur after conducting rubber is stretched and released. Observations of that type were made during the present investigations, and were considered worth recording here since an empirical relationship was found that permits a tabulation of the results.

Figure 6 represents a typical curve of resistance as a function of time after
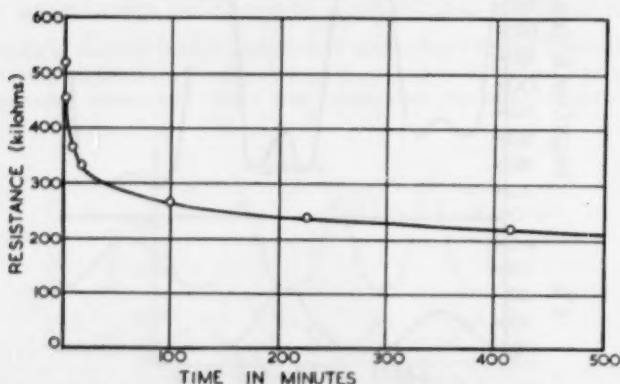
FIG. 6.—Resistance as a function of time at 25° C after stretching and releasing a testpiece of natural rubber containing 50 parts of Philblack O per hundred of rubber.

stretching a testpiece to 20 per cent extension, holding for 1 second, and then releasing. Figure 7 shows a graph $\log_{10}(R - R_0)$ vs. $\log_{10}t$, where R is the resistance at a time t, and R_0 is the resistance before stretching. The linearity of this graph shows that the results can be described by the equation

$$\left(\frac{R - R_0}{R_0}\right)^n = \frac{C}{t} \tag{1}$$

where C and n are constants.

Table II shows the results analyzed in terms of Equation (1) of a series of experiments with various blacks at a temperature of 25° C. From the long duration of these recovery times it is clear that the past strain history is important in determining the resistance of electrically conducting rubber. The strain history of the samples used in these experiments after their removal from
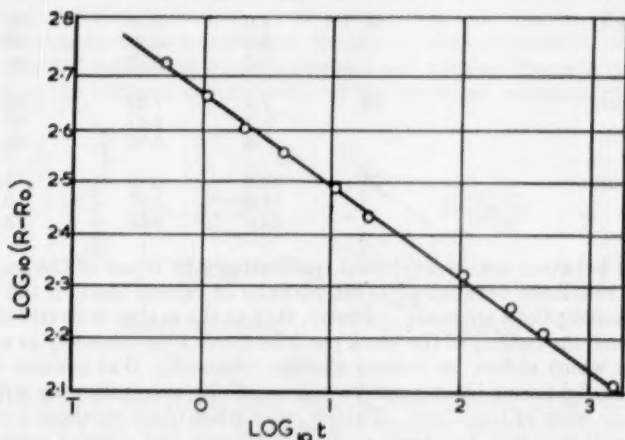
Fig. 7.—Data from Figure 6 replotted. R_0 is the initial resistance in kilohms. R is the resistance in kilohms at time t in minutes.

the mold consisted in storing for about a year followed by cutting individual testpieces from a rubber sheet. The testpieces were heated to 95° C for 1 hour to remove as far as possible the effects of this strain history. Results were also obtained with a compound loaded with Spheron C black. In this case the graph of $\log_{10}(R - R_0)$ against $\log_{10}t$ showed slight curvature which prohibited simple tabulation of the results.

Table III contains the results analyzed in terms of Equation (1) of a series of experiments using the same compound (fifty parts of Philblack O per hundred of rubber) at different temperatures.

DISCUSSION

In general, the resistance of a black-loaded rubber rises when the rubber is first stretched. If the rubber is then repeatedly stretched and released without being left in the unstretched position, then its resistance at first drops and then rises with extension. If the material is left unstretched then its resistance gradually returns towards its initial value at a rate that increases as the temperature is raised.

TABLE II

RESISTANCE RECOVERY DATA AFTER STRETCHING TO 20 PER CENT
EXTENSION FOR ONE SECOND AND THEN RELEASING

Black	Loading per hundred parts natural rubber	n	$Log_{10}C$ (C in mins.)	R_0 kilohms
Dunlop high conductivity	32	4.4	5.00	720
		4.0	4.72	1040
Dunlop high conductivity	70	8.0	6.11	1.4
		7.1	4.78	1.3
		7.5	5.63	1.3
Philblack O	32	4.1	5.50	700
		4.4	5.42	770
		4.8	4.85	840
Philblack O	70	7.0	5.60	18
		5.0	4.63	28
		5.2	5.12	23
Shawinigan	32	7.5	7.29	59
		8.0	8.37	48
		7.3	6.85	59
Shawinigan	70	11.0	6.15	1.0
		11.6	5.37	0.9
		12.6	6.53	1.1

This behavior can be explained qualitatively in terms of the variation of
contact resistance between adjacent particles of carbon black, if the three fol-
lowing assumptions are made. Firstly, that as the rubber is stretched to small
extensions, the centers of the black particles move approximately as points in a
medium which suffers no volume change. Secondly, that contact resistance
between neighboring black particles will be infinite unless they are within a few
Angstrom units of touching[6]. Thirdly, that when black particles are touching
or are within a few Angstrom units of touching, the contact resistance will
decrease as the centers of the particles are pushed together.

Consider two touching black particles forming an element in a conducting
electrical path. Suppose their centers are A and B of a triangle ABC with

TABLE III

RESISTANCE RECOVERY DATA AT VARIOUS TEMPERATURES AFTER
STRETCHING TO 20 PER CENT EXTENSION FOR ONE SECOND
AND THEN RELEASING

Temp. °C	n	R_0 kilohms	$Log_{10}C$ C in mins.
25.6	6.3	54	5.32
	5.7	54	5.45
40.0	5.7	51	4.42
	5.8	58	3.92
	5.0	57	3.86
60.4	4.9	56	2.65
	4.5	55	2.99
	4.8	49	3.13
77.5	4.6	77	2.47
	4.6	73	2.54

ACB a right angle and $CAB = \theta$. Let $AC = 1$, $CB = \tan \theta$, $(AB)^2 = 1 + \tan^2 \theta$.

Assume that the points A, B, and C are points in a material which suffers no volume change on stretching. Suppose the material is stretched along AC and that after stretching, the points A, B, and C become A', B', and C' respectively (Figure 8). If $A'C' = \alpha$, then since there is no volume change

$$C^1 B^1 = \frac{CB}{\sqrt{\alpha}} = \frac{\tan \theta}{\sqrt{\alpha}}, \text{ and } (A^1 B^1)^2 = \alpha^2 + \frac{\tan^2 \theta}{\alpha} \tag{2}$$

From Equation (2) $A^1 B^1$ has a minimum value at $\alpha = \left(\frac{\tan^2 \theta}{2} \right)^{\frac{1}{3}}$ which occurs at values of α greater than unity for values of θ greater than 55°. Therefore, for values of θ greater than 55°, $A'B'$ at first decreases on extension, reaches a minimum, and then increases. If we assume that a decrease in $A'B'$ represents a decrease in contact resistance, we can see that contacts for which θ is greater than 55° suffer first of all a decrease and then an increase in contact resistance as the material is stretched. If the electrical resistance of the ma-
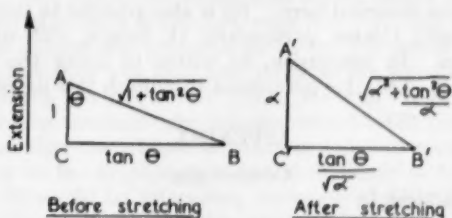
Fig. 8.

terial is made up of numbers of such contacts, then ignoring for the time being contacts having θ less than 55°, it can be seen that the resistance should at first drop and then rise as the material is stretched. Those contacts for which θ is less than 55° are pulled apart and tend to open as soon as the material is stretched. The large increase of resistance on first stretching the rubber may be attributed to breaking some of these contacts. After a contact is opened, then it stays open and does not contribute to the conductivity until the separation between the particles is reduced to a few Angstrom units. Mullins[7] has investigated the phenomenon of permanent set in black-loaded natural rubber, and shown that this is a slow return of the material to the dimensions it possessed before it was stretched. Therefore, all of the contacts for which θ is less than 55° and which are opened by stretching will not be closed as soon as the sample is released. However, as the sample regains its initial geometry, more and more contacts will return to within a few Angstrom units of their initial positions and will close.

This theory therefore suggests that the initial resistance increase on first stretching black-loaded rubbers is due to opening completely some of those contacts that have values of θ less than 55°. It is suggested that the cyclic experimental results are due to changes in the contact resistance of contacts having θ greater than 55°. The recovery of the initial resistance after stretching and releasing is thought to be due to contacts closing as the rubber regains its initial dimensions.

It is not suggested that the theory outlined above provides an exact analysis of the mechanism of the resistance changes in conducting rubber. The first assumption on which it is based, that the centers of carbon black particles move as points in a material suffering no volume change, has some obvious limitations; as the carbon black particles are pushed together they will, in general, not deform sufficiently to satisfy this condition. The theory outlined does not specify whether the carbon black particles considered are individual particles or whether they are clusters of particles. However, this theory does indicate how a complex mass of information may possibly be reconciled with a simple geometrical picture.

It can be seen from this work that the result of Kersta[6] that Thiokol LP-2 loaded with carbon black sometimes exhibits a decrease of resistance on stretching is not as surprising as it at first appeared. It is possible that the observations may have been carried out after a prestress from which the Thiokol with its large amount of permanent set had not had time to recover.

ACKNOWLEDGMENTS

The author is indebted to J. G. Smith who carried out many of the experimental observations recorded here. He is also grateful to the many people at the Dunlop Research Center, particularly D. Bulgin, with whom he has had helpful discussions. In conclusion, he wishes to thank the directors of the Dunlop Rubber Co., Ltd., for permission to publish this paper.

APPENDIX

Compounds

Thiokol FA + Philblack O.

    Thiokol FA 100; zinc oxide, 10; stearic acid, 0.5; dibenzothiazolyl disulfide, 0.3; diphenylguanidine, 0.1; Philblack O, 50.
    Vulcanized 15 mins. rise followed by 40 mins. at 148° C.

Neoprene + Philblack O.

    Neoprene, 100; magnesia, 4; zinc oxide, 5; dibenzothiazolyl disulfide, 1; mineral oil, 4; stearic acid, 1; Philblack O, 50.
    Vulcanized 15 mins. rise followed by 60 mins. at 142° C.

Butyl Rubber + Philblack O.

    Butyl rubber, 100; sulfur, 2; mercaptobenzothiazole, 0.5; tetramethylthiuram disulfide, 1.0; stearic acid, 2; zinc oxide, 5; Philblack O, 50.
    Vulcanized 15 mins. rise followed by 100 mins. at 148° C.

Natural Rubber.

    Rubber, 100; sulfur, 3; mercaptobenzothiazole, 1; zinc oxide, 5; stearic acid, 3; Nonox HFN, 1; varying amounts of black specified in text.
    Vulcanized 15 mins. rise followed by 50 mins. at 138° C.

CONFERENCE DISCUSSION

Dr. Gordon said he wished to refer to the very last few remarks that Dr. Marshall had made, i.e., to the kinetics of relaxation which were very adequately covered in his paper by Equation (1) and the beautifully linear plot in Figure 7. Not very much theory was given for that in the discussion at the end of the

paper, and he thought that while probably no one could give a complete kinetic interpretation one could go a little further.   It was perhaps significant that the law of Equation (1) could be transformed by differentiation into the form which in chemistry was known as the law of mass action, i.e., the rate D was proportional to the $(n + 1)$th power of x.   In chemistry x was a concentration of some species, but in this case x was the difference between current resistance R and the final (or initial) resistance R_0.   It was very significant also that the so-called order n was very high, ranging from about 4 to 12.

Some years ago he had studied the relaxation kinetics not in terms of the electrical resistance but the volume change of a rubber, reinforced not with carbon black but with cyclized rubber.   In his view it was important that the law which Dr. Marshall had found was also obeyed when x represented the remaining volume change and not the remaining change in electrical resistance. In his own case n, or the reaction order, was 5, which was very nearly the lower limit of Dr. Marshall's figures.

The conclusion in the case of the relaxation behavior in terms of volume change was perhaps easier to draw than it was in the case of electrical resistance. First of all when one stretched the reinforced rubber it was well known that the volume increased, and it was the subsequent return to the original state that obeyed exactly the same type of chemical mass law.   In that case it meant that rate of change of volume was proportional to the 5th power of the remaining volume change, and that was the same thing as the separation between the molecules following a 5th power rate law.   One well knew that the van der Waals forces between the molecules followed about a 6th power law.   Therefore one could see that the relaxation behavior followed roughly the law that the rate of return to the original state varied inversely as the forces between the molecules.   It would be interesting to know whether Dr. Marshall had given any thought to such mechanistic interpretations of his kinetic measurements.

Dr. Marshall, in reply, said he was fascinated by Dr. Gordon's remarks. He had in fact reflected on the kinetic mechanisms but he was a little chary about going too far because in the electrical case there was an unfortunate missing link in the process.   One had to get from resistance to a concentration, which one perhaps could do from loading curves, but the difficulty of getting good experimental data from loading curves was rather great.

There was one feature which he had not included in the paper but which was relevant to Dr. Gordon's remarks.   If one considered Table III, in which the log C was some measure of the recovery time, and if log C was plotted as a function of the reciprocal of the absolute temperature one got a fairly linear plot from the results listed.   If one was so bold as to deduce the activation energy from that, the answer came out to be about 30 kilocalories per gram molecule.

Mr. Mullins regarded it as quite clear that the mechanism put forward will qualitatively give effects of the type observed.   However, Dr. Marshall had considered only conduction between spherical particles of black, and we have grown to think of fine particle blacks in rubber existing as anisotropic chains or agglomerates.   It is not immediately obvious what effect orientation by stretching has on the conductivity of rubbers containing anisotropic particles of black, but the effects may be considerable and have been previously invoked to describe changes in conductivity occurring on extension.   Plausibly they could give a basically similar picture.   He was curious to know why Dr. Marshall had not discussed the possible contribution of orientation.

Dr. MARSHALL, in reply, said the question of orientation of black particles in rubber was one way of looking at the problem, but from the point of view of conductivity one probably obtained a more clear picture in terms of contact resistance. He thought Mr. Mullins' approach and his own were actually identical in the sense that if one thought in terms of specific resistance then one had to think in terms of orientation; if one thought in terms of sample resistance then one had to think in terms of contact resistance. He had thought in terms of sample resistance because he considered conduction through electrically-conducting rubber to be more like conduction through a chain of radio resistors hidden in a bicycle inner tube than conduction through an isotropic material. Actually it was a matter of choice whether one thought in terms of sample resistance and then started thinking of all the contacts which went to make up the sample resistance, or whether one thought of specific resistance and then started thinking of the distribution of black which resulted in the specific resistance.

Dr. DANNENBERG said in a recently published paper (*Ind. Eng. Chem.* **46**, 218, 1954), he had described the very interesting phenomenon of a resistance maximum as a function of elongation for a highly conductive natural rubber compound, and had mentioned in this paper another reference (*J. Applied Physics*, **18**, 456, 1947), where the same phenomenon had been observed. It was noted that the resistance attained a maximum value at 25 to 125 per cent elongation, depending on the compound, and beyond this elongation up to about 150 per cent the resistance continually decreased. He wondered whether Dr. Marshall was familiar with this work, and could perhaps comment on it from the standpoint of his proposed mechanism of contact resistance.

Dr. MARSHALL replied that he was certainly familiar with the paper in question but had not included any reference to it in his own paper because the text of it was not available in this country until it was published in *Industrial and Engineering Chemistry* in January of 1954, which was after he had submitted his paper. He believed he was right in thinking that the maximum published by the previous speaker was not a maximum in resistance but a maximum in resistivity, and he had given both resistance as a function of extension and resistivity as a function of expansion. The resistance had no maximum but the resistivity had. The question of whether to try to interpret results in resistivity or resistance was a matter of whether one thought the problem of conduction through rubber was more like the problem of conduction through a chain of resistors concealed from view inside an extensible inner tube, or whether it was more like the problem of conduction through an isotropic material. He personally thought it was the former, and so preferred to think in terms of sample resistance, but he believed he was right in saying that in terms of sample resistance the previous speaker's data did not show the maximum.

Dr. DANNENBERG apologized for not remembering the data in such detail but said he could assure Dr. Marshall that the absolute resistance itself had gone through a maximum and of course the specific resistivity also would go through the maximum. Perhaps the paper as it has been given did not emphasize this point, but he had done many tests and could say that as a general rule for conductive rubber stocks the absolute resistance did go to a maximum. It depended on the rate of extension, and he had tried to check the effect of rate extension from 250 per cent to 25 per cent per minute, and in both cases that phenonenon had been observed. If one slowed down the extension rate below the 25 per cent per minute one would perhaps eventually come to the point where one would see no maximum. In his view it was very time-dependent.

Dr. MARSHALL said he was very interested in the last remarks.   Under the conditions of his own experiments he had never seen the maximum of resistance but that might well be a question of how fast one did the experiment.   It would not be unduly surprising, in that the point of view he was trying to put across was that there were two processes going on: the lateral kind of sideways movements and the other effect along the direction of stretch, and what actually happened was a balance of those two.   He could only say that on the face of it it might be possible to reconcile those results with his point of view.

A DELEGATE asked whether Dr. Marshall would agree that there was probably a third process involved, namely a weak flocculation of the carbon particles to give rise to increased conductivity at the same time as the mechanical effects were going on because if one stopped the extension at any given point one would immediately be stopping the stretch of the sample and in its elongated condition the conductivity immediately began to increase.

Dr. MARSHALL in reply, said there might well be flocculation but he was not certain that it was necessary to invoke it to explain the results obtained, because as soon as the sample retracted to its original extension in the unstretched position then in terms of his mechanism the contacts that were initially open began to close, so that the resistance would return to its initial value.   The thing that made him a bit skeptical about flocculation was that in his observations in which the detailed cyclic behavior was observed rather than the resistance at the moment of stopping the experiment, it had been found that in some cases the 10,000th cycle resistance curve was virtually identical with the first.   If there was very much flocculation going on it would be rather difficult to imagine such consistent results.

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RUPTURE OF RUBBER. IV. TEAR PROPERTIES OF VULCANIZATES CONTAINING CARBON BLACK *

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INTRODUCTION

A method of studying tear behavior has been described in a previous paper[1] (Part III, subsequently referred to as III), and was illustrated by results obtained with natural rubber and GR-S gum vulcanizates, i.e., vulcanizates containing no added ingredients apart from those necessary for vulcanization. In the present paper the method is applied to vulcanizates containing different types of carbon black. Vulcanizates of this type are of considerable interest, since the carbon black can appreciably modify physical properties such as stiffness and tensile strength and can induce pronounced anisotropy in tearing, referred to by Buist[2] as knotty tearing.

EXPERIMENTAL

1. THE VULCANIZATES

The compounding recipes and the times and temperatures of cure of the vulcanizates employed are given in the Appendix. Each vulcanizate was molded in the form of sheets about 1 mm. thick, from which the tear test pieces were cut. Polysar S, polymerized at 50° C, with 23.5 per cent bound styrene, was used for the GR-S vulcanizates. Three types of carbon black were employed—High Abrasion Furnace (HAF), Fine Thermal (FT), and Medium Thermal (MT), in order of increasing particle size[3].

The GR-S vulcanizates A, B, and C, containing HAF, FT, and MT blacks, respectively, have been compared with two gum vulcanizates D and X, of different degree of vulcanization. The vulcanizing recipe and curing conditions for A, B, and C were the same as for D. Similarly, the natural rubber vulcanizates E, F, and G, containing HAF, FT, and MT blacks, respectively, have been compared with two gum vulcanizates H and Y, of different degree of vulcanisation. The vulcanizing recipe and curing conditions for E, F, and G were the same as for H. It would be expected that A, B, C, and D would differ in degree of vulcanization, and likewise E, F, G, and H[3]. It is for this reason that two gum vulcanizates have been used in each case for comparison. The gum vulcanizates X and Y were those referred to in III as A and E, respectively, and the results given there have been used, with minor additions, for the present investigation.

The tensile strength and elongation at break for each of the above vulcanizates are given in Table I. The data were obtained at 20° C on dumbbell specimens with a Goodbrand tensometer, the speed of the machine being 20 inches/minute. Table II gives the elastic constants C_1 and C_2 for the gum

TABLE I

Vulcanizate	Rubber	Black	Tensile strength, kg./cm.^{2}	Elongation at break, %
A	GR-S	HAF	230	410
B	GR-S	FT	130	650
C	GR-S	MT	115	630
D	GR-S	—	21	410
X	GR-S	—	23	200
E	Natural	HAF	245	370
F	Natural	FT	205	580
G	Natural	MT	190	520
H	Natural	—	235	710
Y	Natural	—	240	830

vulcanizates D, X, H, and Y.   The method of deriving these constants from stress-strain measurements has been indicated in III; C_1 provides an approximate measure of the degree of vulcanization.

2. METHOD OF MEASUREMENT AND TYPES OF TEARING

The tear behavior of the vulcanizates was investigated by measuring the energy for tearing T for various rates of propagation, T being defined as the energy expended per unit increase in the length of the tear for unit thickness of the test piece.   For the type of test piece employed, T can be derived directly from the applied tearing force and the rate of propagation can be obtained from the rate of extension of the test piece.   The principal method of measurement (the extensometer method) was to extend test pieces at various uniform rates and measure the tearing force.   Rates of propagation in the range 2.5×10^{-4} to 25 cm./sec. were covered in this way.   In certain instances the converse method, in which various tearing forces were applied and the rates of propagation were measured, was used to extend the range to lower rates of propagation, or to ascertain what tearing, if any, occurred at low values of T.   Full details of the methods of measurement, and of the type of test piece, have been given in III.

As discussed in III, tearing can be classified as steady or stick slip, according to the effects observed with the extensometer method.   Steady tearing is associated with a positive or, as a limiting case, a zero gradient in the tearing-energy rate of propagation relation for the rubber, and stick slip tearing is associated with a negative gradient.   In the latter case, the extensometer method can be used to ascertain the dependence of T on the rate of propagation, but not the converse (constant force) method.

The tearing observed with carbon-filled vulcanizates conforms to the above classification.   However, as mentioned in the Introduction, these vulcanizates can exhibit distinctive features, both in the appearance of the torn surfaces and in the manner in which the tear progresses, which are directly indicative of anisotropy.   Pronounced anisotropy in tearing is associated with stick slip

TABLE II

Vulcanizate	Rubber	C_1, kg./cm.^{2}	C_2, kg./cm.^{2}
D	GR-S	1.2	1.5
X	GR-S	2.3	1.7
H	Natural	1.5	1.1
Y	Natural	1.2	1.1
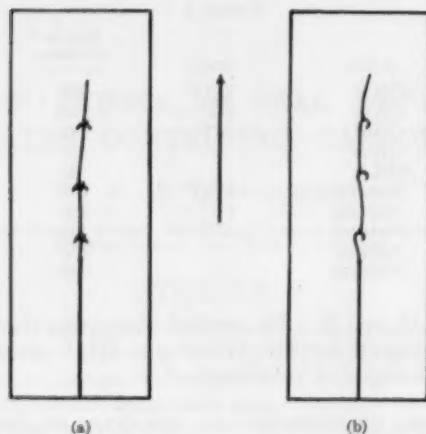
Fig. 1.—Forms of knotty tearing. The arrow indicates the direction of tearing.

behavior and enhanced tear resistance, and will be referred to as knotty tearing.

The distinguishing features of knotty tearing are best illustrated by the effects observed when a test piece is extended at a uniform rate. When stick slip tearing occurs, the tearing force and rate of propagation undergo a regular cycle of fluctuation, and the part of the cycle in which the rate is low is associated with an increase of the tearing force to a maximum, at which point the rate of propagation increases rapidly and the tearing force relaxes. Subsequently,
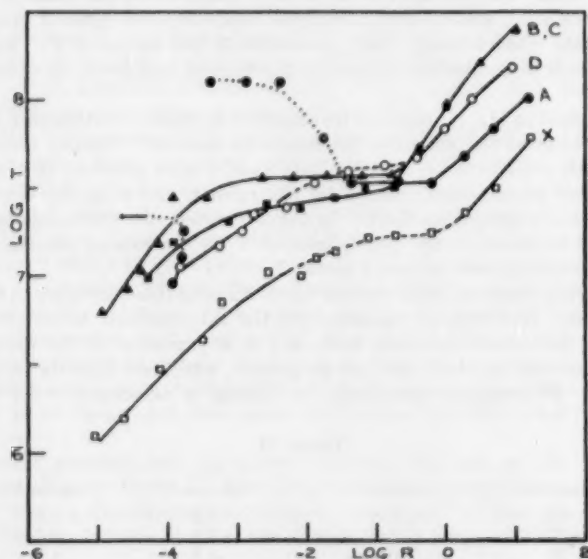
Fig. 2(a). −20° C.
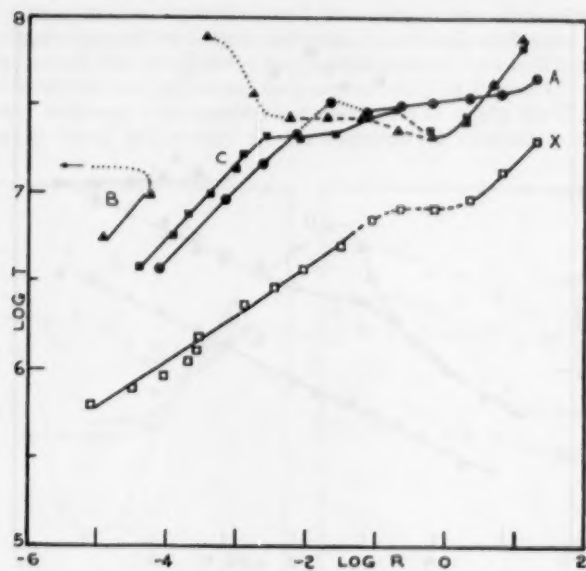
Fig. 2(b).   0°C.   See legend under (c).

Fig. 2(c).   25° C.
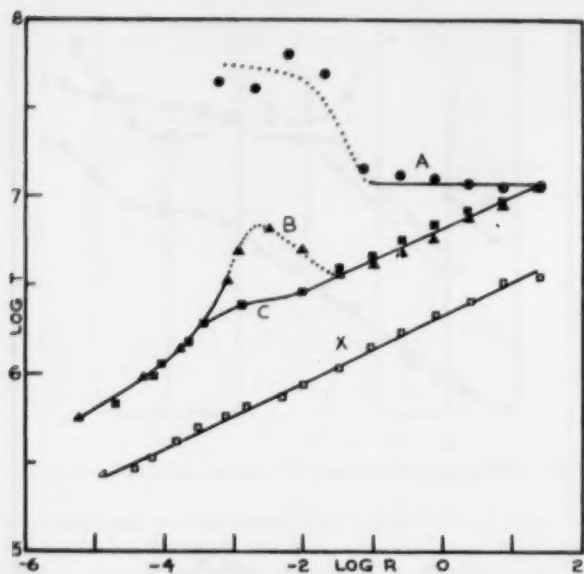
Fig. 2(d). 50° C. See legend under (e).
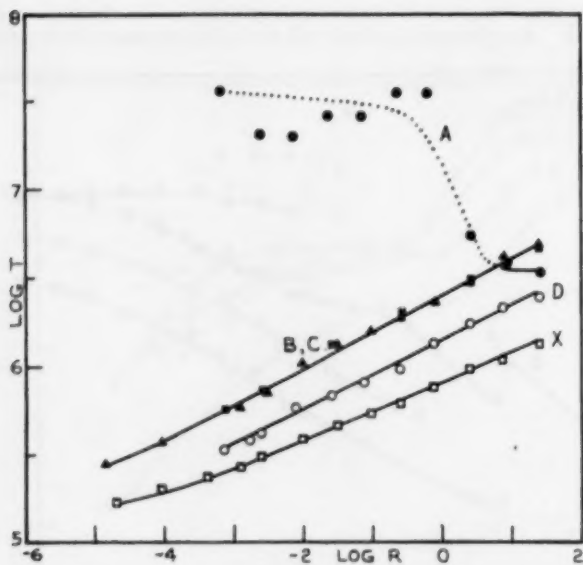
Fig. 2(e). 90° C.

Fig. 2.—Tearing energy T in ergs/cm.^{2} vs. rate of propagation R in cm./sec. for GR-S vulcanizates A(HAF black), B(FT black), C(MT black), D, and X(gum). Steady, stick slip, and knotty tearing are shown by full, broken, and dotted lines, respectively.

the rate of propagation diminishes and the cycle is repeated (cf. III).   The
slow propagation part of each cycle coincides, in general, with some irregularity
of the torn surface, but with knotty tearing it is marked by a well defined lateral
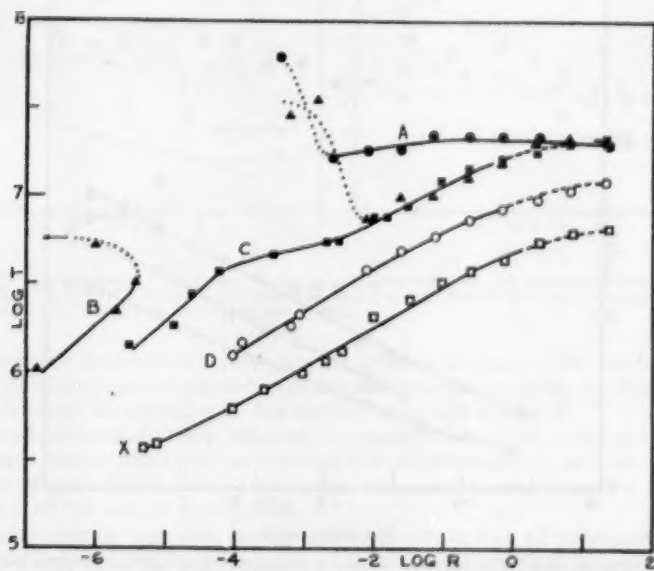development of the tear, as shown diagrammatically in Figure 1.   The lateral
development increases considerably the effective size of the tip of the tear so
that a higher force, and energy T, are required for continued propagation.
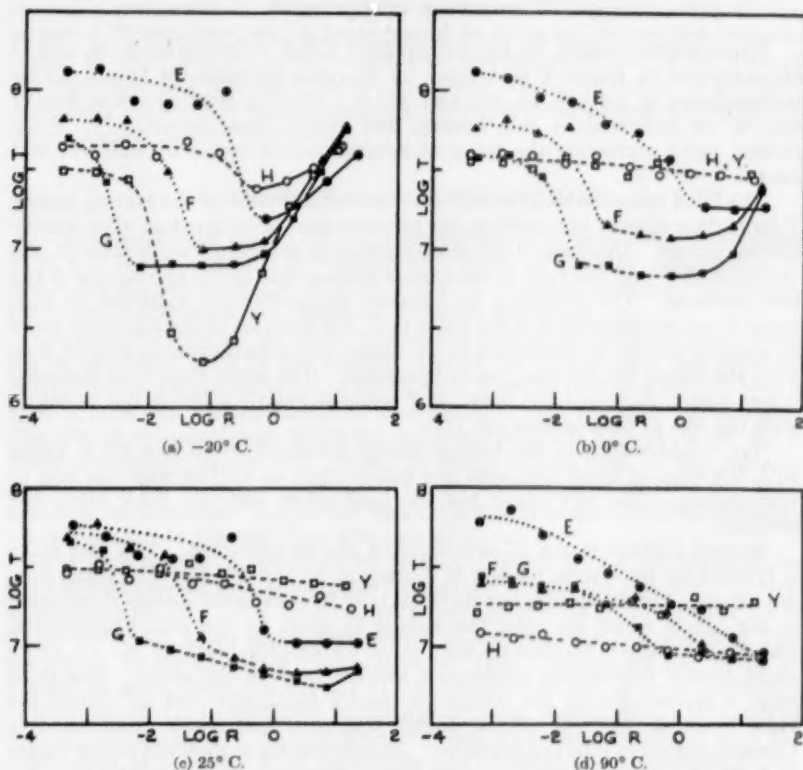
Fig. 3.—Tearing energy T in ergs/cm.² vs. rate of propagation R in cm./sec. for natural rubber vulcani-
zates E(HAF black), F(FT black), G(MT black), H, and Y(gum).   Steady, stick slip, and knotty tearing
re shown by full, broken, and dotted lines, respectively.

The stick slip behavior in knotty tearing arises principally from the fact that
if the rate of propagation increases the lateral development of the tip diminishes,
with a consequent reduction in the tearing force, and energy T.

For all forms of stick slip behavior, the energy T has been derived from the
maximum tearing force and the average rate of propagation, as derived from
the rate of extension of the test piece, has been used in describing the depend-
ence of T on the rate of propagation.

Knotty tearing does not develop above a certain rate of propagation, the
transition from knotty to other types of tearing being marked by a reduction
in the value of T.   For rates of propagation well below the transition, knotty

tearing develops in the form shown in Figure 1a, but for intermediate rates the form shown in Figure 1b may be observed. This change in form is accompanied by a change in the size of the tip of the tear and is responsible for much of the apparent scatter in the results given in Figures 2 and 3.

RESULTS

3. THE GR–S VULCANIZATES

Experimental results for the carbon-filled GR-S vulcanizates A, B, and C are compared in Figure 2 with those for the gum vulcanizates D and X, for temperatures of −20, 0, 25, 50, and 90° C. Steady, stick slip, and knotty tearing are indicated by full, broken, and dotted lines, respectively. Each plotted point represents the mean of several measurements on different test pieces.

The filled vulcanizates generally show an enhancement of the tearing energy T for certain rates of propagation, the enhancement being greatest when knotty tearing occurs. Otherwise they closely simulate the gum vulcanizates in the variation of T with the rate, in the type of tearing, and in the appearance of the torn surfaces. The similarity in behavior is particularly apparent at high rates; there are differences in the value of T, but they are of the kind that could be ascribed simply to differences in the degree of vulcanization, as may be seen from the curves for the two gum vulcanizates. The latter show that increased vulcanization decreases the value of T without greatly altering the variation with the rate of propagation (cf. III).

The enhancement of the tearing energy produced by carbon black varies with the type of black and with the temperature as well as with the rate of propagation. The MT black has the least effect and the HAF black the greatest.

Several distinct stages of enhancement can be identified. The first stage is typified by the curves for the MT black at 25 and 50° C. The black does not produce knotty tearing but its effect may be seen in the humps it produces in the curves which are otherwise similar to those for the gum vulcanizates. The second stage is typified by the results for the FT black at 50° C, where slight knotty tearing has produced a distinct peak in the curve. The third stage is represented by the curves for the FT black at 0 and 25° C and the HAF black at −20° C. Here, knotty tearing is sufficiently pronounced to separate the curve into two branches. Steady tearing is observed at low values of T (the lower branch of the curve), but as T is increased tearing tends to become knotty and for the value of T indicated by the arrow in Figures 2a, b, and c the resultant enlargement of the tip of the tear is sufficient to reduce the rate of propagation virtually to zero. A considerably higher value of T, as shown by the upper branch of the curve, is then required for continuous propagation.

Evidently a certain value of $T(T')$ must be exceeded for knotty tearing to occur. The curves indicate that for low rates of propagation, e.g., 10^{-6} cm./sec., either knotty or steady tearing may occur, depending on whether or not T' is exceeded in attaining the given rate of propagation. If the desired low rate of propagation is approached asymptotically from below, by extending the test piece at the appropriate uniform rate or by applying a suitable small load, then steady tearing will occur, with a value of T corresponding to the lower branch of the curve. If, however, the test piece is extended at a high rate initially so that T' is exceeded, then the rate of propagation may be subsequently reduced

to the desired value and knotty tearing will occur, with a value of T corresponding to the upper branch of the curve.

The final stage in the enhancement of tear resistance may be considered as one in which the lower branch of the curve is displaced to very low rates of propagation to become virtually inaccessible to observation. This stage is approached by the HAF black at 25, 50, and 90° C, where knotty tearing is pronounced and only the upper branch of the curve is apparent within the normal experimental range of rates of propagation. Steady tearing at low values of T, associated with a lower branch to the curve, has in fact been observed at 25° C, but the rate of propagation was extremely low, of the order of 10^{-3} cm./sec. At this stage, where the lower branch of the curve becomes practically inaccessible to observation, a filled GR-S vulcanizate is comparable with a natural rubber vulcanizate.

4. THE NATURAL RUBBER VULCANIZATES

The experimental results for the carbon-filled natural rubber vulcanizates E, F, and G are compared in Figure 3 with those for the gum vulcanizates H and Y, for temperatures of −20, 0, 25, and 90° C. Again, each point represents the mean of several measurements on different test pieces.

At each temperature the filled vulcanizates exhibit pronounced knotty tearing at the lower rates of propagation, and at the higher rates the behavior reverts, with an appreciable fall in the value of T, either to steady tearing or to a type of stick slip tearing similar to that observed with the gum vulcanizates. The rate of propagation at which the transition occurs is highest for the HAF black and lowest for the MT black. It would appear that for low rates of propagation the energy T approaches a high limiting value in both the filled and gum vulcanizates. In contrast with the behavior of the GR-S vulcanizates, a lower branch to the curve has not been observed.

For high rates of propagation at −20° C (Figure 3a) all the vulcanizates show steady tearing with appreciable increases of T with the rate, and the torn surfaces are similar. The comparatively small differences in the value of T are of the kind that could be ascribed simply to differences in the degree of vulcanization, as for the GR-S vulcanizates (cf. III). Comparing the results of Figure 3a with those for the GR-S vulcanizates at the same temperature (Figure 2a), it will be seen that, at the highest rates of propagation, the curves for the vulcanizates E, F, G, and H are arranged in the same order and show the same trend as those for A, B, C, and D. In addition, the appearance of the torn surfaces is similar in all cases.

For the higher rates of propagation at the higher temperatures (Figure 3b, c, d) the vulcanizates again show some similarity of behavior in the zero or negative slope to the curves. The curves for the filled vulcanizates generally lie below those for the gum vulcanizates, however, in contrast with the order observed at −20° C for high rates. This point is discussed in Section 6.

DISCUSSION

5. TEAR PROCESSES

The experimental results suggest a common pattern of behavior for all the vulcanizates, and the complexity of the curves, the different types of tearing, and the changes in the appearance of the torn surfaces indicate that several

processes are involved.   The behavior can be accounted for by a combination
of a common basic process with one or more secondary processes of an essenti-
ally similar type.

The basic process is associated with a continuous increase of the energy T
with the rate of propagation, a variation which would be expected, *a priori*,
for an irreversible process such as tearing[1,4].   The secondary type of process is
associated with the converse variation, i.e., with a decrease of T with the rate of
propagation.   As discussed in III, this process is attributed to a strengthening
structure (e.g., crystallization), developed by extension of the rubber at the tip
of the tear, which requires a finite time to form and which consequently does not
develop at high rates of propagation.   Although the time required for structure
formation would be expected to vary with the vulcanizate and the temperature,
all vulcanizates should show a similarity in behavior at sufficiently high rates of
propagation, when only the basic process is operative.

The decrease of T with the rate of propagation and the accompanying stick
slip tearing associated with a strengthening structure may be masked by the
opposite effect of the basic process.   The presence of a secondary process is
therefore to be inferred, more generally, from pronounced changes in the slope
of the tear curves and associated changes in the appearance of the torn surfaces.

The behavior of the gum vulcanizates can be described in terms of the basic
process in combination with a single secondary process involving a strengthen-
ing structure attributed to the crystallization produced by extension of the rub-
ber.   The latter is the predominant process with the natural rubber gum vul-
canizates over the experimental range of rate and temperature, in contrast with
GR-S, where the basic process is predominant.   In the filled vulcanizates there
is an additional secondary process involving the strengthening structure con-
tributed by carbon black.   The influence of the carbon black structure is more
readily apparent in the GR-S vulcanizates because its effects are not obscured
by those of crystallization.

The manner in which the tearing energy depends on the strength of the
rubber and on the size of the tip of the tear is shown by the relation

$$T \approx d E \tag{1}$$

derived by Thomas[4] for an incision with a semicircular tip of diameter d, E
being the work to break/unit volume for the rubber in simple extension (at the
tip of an incision, or tear, the rubber is in simple extension).   The effective
diameter d for a tear will be governed by the degree of irregularity, or lateral
development, of the tip and may vary with the rate of propagation, as in knotty
tearing. E is a function of rate of extension, the rate of extension at the tip
of the tear being governed by the rate of propagation.   Both d and E may con-
tribute to the variation of the tearing energy T when a strengthening structure
is present, but where the basic tear process predominates, as in the GR-S gum
vulcanizates, the variation in E appears to be the more important, as shown by
a comparison of tear measurements with the data of Dogadkin and Sando-
mirskii[5] on the variation with rate of extension of the tensile strength and
elongation at break of GR-S gum vulcanizates.   The variation of E with rate
of extension, as derived from the data, is sufficient to account for the variation
of T with the rate of propagation.

Such a comparison of tear and tensile rupture measurements indicates that
in the basic tear process the stress and extension at the tip both increase with

the rate of propagation. This will influence the development of a strengthening structure, for the amount of structure may be expected to increase with the extension (or stress) at the tip. The rate of extension at the tip, also governed by the rate of propagation, has the opposite effect, so that in suitable instances a maximum of structure development should be apparent for a particular rate of propagation. This expectation is borne out by the experimental results, notably those for the GR-S filled vulcanizates. If the structure develops at low extensions, the maximum will be shifted to low rates of propagation and may be unobservable in practice, as would appear to be the case, for example, with the natural rubber vulcanizates.
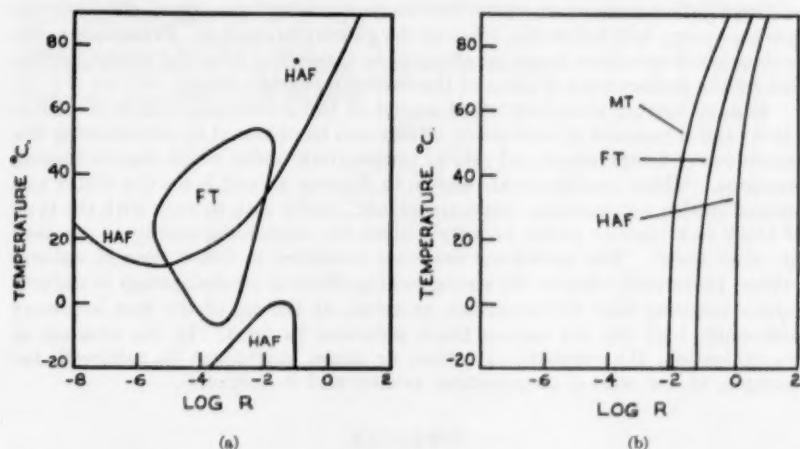

Fig. 4.—Conditions of temperature and rate of propagation R (in cm./sec.) for knotty tearing: (a) GR-S vulcanizates containing HAF and FT black. The conditions occur within the closed or partially closed curves. (b) Natural rubber vulcanizates containing HAF, FT, and MT black. The conditions occur to the left of the appropriate curve.

6. INFLUENCE OF CARBON BLACK ON TEAR BEHAVIOR

The introduction of a filler may influence tear behavior in three ways: (1) by influencing the basic tear process, (2) by affecting crystallization, and (3) by contributing a strengthening structure. The results for the GR-S vulcanizates, as well as those for the natural rubber vulcanizates at high rates at low temperatures, indicate that the net effect of carbon black on the basic tear process is comparatively small, allowing for some uncertainty as to the degree of vulcanization of the filled rubbers. It is also apparent that the ability to crystallize is not radically altered, for features attributed to crystallization in the curves for the gum vulcanizates can also be traced in the curves for the filled compounds. This is in agreement with x-ray diffraction[6] and stress relaxation measurements[7] on natural rubber vulcanizates. The main effect of carbon black thus appears to be the contribution of a strengthening structure.

Equation (1) shows that a strengthening structure may increase the tearing energy both by increasing d, the effective diameter of the tip of the tear, and by increasing E, the work to break/unit volume. In the case of carbon black structure, the more obvious is the increase in d, associated with knotty tearing;

in the transition from knotty to other forms of tearing, d changes by a factor of about 10. The effect of an increase in E due to the formation of a carbon black structure tends to be obscured by knotty tearing, and also, in the natural rubber vulcanizates, by the increase in E due to crystallization. Knotty tearing does not occur with the MT black in GR-S, however, and the increased tearing energy observed at certain rates of propagation can be attributed to an increase in E. In several instances with the HAF black in GR-S, the strengthening effect of the carbon black structure can be seen to persist at rates of propagation above the knotty tearing transition, and this may likewise be attributed to the increase in E. The appearance of the torn surfaces indicates that, with the natural rubber vulcanizates also, the carbon black structure still persists at rates of propagation somewhat above the knotty tearing transition, although the tearing energy falls below the value of the gum vulcanizates. Presumably, the carbon black structure is not so effective in increasing E as the crystallization lost by the replacement of some of the rubber by carbon black.

Knotty tearing is an important aspect of the reinforcing action of carbon black, and a measure of reinforcing ability can be obtained by determining the conditions of temperature and rate of propagation under which knotty tearing develops. These conditions are shown in Figures 4a and b for the GR-S and natural rubber vulcanizates, respectively, and can be seen to vary with the type of black in a manner which broadly follows the reinforcing ability as assessed by other tests[2]. The conditions are more restricted in GR-S than in natural rubber, presumably due to the strengthening effect of crystallization in natural rubber ensuring that the extension, or stress, at the tip of the tear is always sufficiently high for the carbon black structure to form. In the absence of crystallization, the requisite extension, or stress, might not be achieved, for example, at low rates of propagation, as discussed in Section 5.

APPENDIX

The compounding details of the vulcanizates were as follows:

Vulcanizate	A, B, C	D	X	E, F, G	H	Y
GR-S (Polysar S)	100	100	100	—	—	—
Natural rubber (smoked sheet)	—	—	—	100	100	100
Carbon black	50	—	—	50	—	—
Sulfur	1.75	1.75	3	3	3	3
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	1	3	3	1
Mercaptobenzothiazole	—	—	1	1	1	0.5
Cyclohexylbenzothiazolyl sulfenamide	1	1	—	—	—	—
Diphenylguanidine	—	—	0.5	—	—	—
Antioxidant	1	1	0.5	1	1	1
Dutrex R	6	—	—	—	—	—
Temperature of cure (° C)	145	145	140	140	140	140
Time of cure (min.)	50	50	40	45	45	45

The types of carbon black used were: Philblack O(HAF), P33(FT), and Thermax (MT).

ACKNOWLEDGMENT

SYNOPSIS

The tear properties of natural rubber and GR-S vulcanizates containing carbon black are compared with those of gum vulcanizates, using a method developed in a previous paper. The distinctive features in the tear behavior of the filled vulcanizates are noted and discussed. The results indicate that there are two types of tear process, which vary in importance according to the tearing conditions, and the influence of carbon black on these processes is discussed.

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NATURE OF CHEMISORPTIVE MECHANISMS IN RUBBER REINFORCEMENT *

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INTRODUCTION

The term "reinforcement" has been largely arbitrary depending on the particular criterion chosen by different investigators for its definition. Thus, an increase in modulus is held by some to be direct evidence for true reinforcement. Others, however, regard abrasion resistance, tear resistance, and tensile strength as the three most important properties associated with reinforcement[1]. In each of these cases the attempt to arrive at a definition of reinforcement is based on rubber tests which again are highly arbitrary, since in this approach to the problem it is impossible to avoid contradictions associated with selection of a particular type of rubber, formula, and conditions of vulcanization. The confusion that exists in this field of rubber research is largely due to the scant information available on the true nature of rubber-filler interaction. One strong school of thought maintains that the strength of bonding depends mainly on van der Waals forces and therefore on particle size[2], although it is admitted that fine particle size alone might not be sufficient to produce reinforcement.

On the other hand, several observations[3] indicate the presence of reactive sites and suggest that strong bonds of a chemical nature form between filler and rubber matrix. Thus, attempts have been made to describe the chemical nature of the surface by such terms[1] as "surface character", referring to adsorbed gases or "oxygen compounds," and "lattice imperfections". All of these, however, have been of but little help in solving the physical versus chemical controversy. From their experiments on the heat of adsorption of bromine on carbon black and simple olefins, Stearns and Johnson[3] tried to obtain new evidence for the chemical nature of the rubber-filler bond. Their evidence, however, has not been accepted as conclusive, since the heat involved is not characteristic of chemical bond formation. Stepwise nitrogen adsorption, as observed by Beebe[3] et al., and also the heats of adsorption for nitrogen and a series of C_4 hydrocarbons showing "initial sites of high activity" might possibly be taken as more conclusive evidence. The most impressive evidence for a chemical rubber-filler interaction is offered by the phenomenon of carbon-gel formation[4]. It appears, however, that those who have investigated gel formation have failed to realize the importance of this effect. Thus some authors have considered that the development of a carbon-gel complex "follows an adsorption path". They have pointed out that increasing fineness of the carbon black, accompanied by expanded adsorbing surface, leads to a greater amount of bound rubber. However, the figures quoted by these authors for carbon-gel formation in GR-S rather indicate the opposite, HAF black forming more gel than EPC black on both cool and hot mixing. From this information it ap-

pears that no general statement can be made as to the relation between particle size of the filler and the amount of carbon gel produced. In Hevea the EPC black with an area greater than HAF black produced more carbon gel, whereas in GR-S 100 the situation was reversed. That the amount of gel formation depends also on temperature follows from Sweitzer's "dry adsorption" experiments. From results obtained with polymers of varying degrees of unsaturation it was also concluded that unsaturation is required for adequate development of the carbon-gel complex. Kolthoff et al.[5], in their experiments of sorption of GR-S type rubber by carbon black at ordinary temperatures in various solvents, observed the same effect, but made no attempt to investigate its reversibility. These experiments, together with Sweitzer's results, would suggest that the effect of gel formation as well as Kolthoff's sorption effects must be, at least in part, of an irreversible character. The extraordinary effect of unsaturation of the polymeric material on the carbon-gel level, as indicated in Sweitzer's paper, cannot possibly be explained by mere physical adsorption. Unsaturation of the polymer also is known to be a necessary condition for effective reinforcement by a carbon filler; saturated polymers such as polyisobutylene cannot be reinforced to any marked degree[6]. Since, then, unsaturation appears to be a dominant feature in both carbon-gel formation and reinforcement, it would appear that reinforcement and gel formation must be inter-related. This has been substantiated by Braendle, Sweitzer et al., who investigated the factor of carbon-gel formation in the reinforcement of synthetic as well as natural rubber[7]. On the other hand, there are also some common features in both reinforcement and vulcanization, e.g., the crystallization effects described by Gehman and others[8]. Naunton and Waring went so far as to suggest that the strong bond between rubber and filler acts like the sulfur bridge in vulcanization with sulfur[9]. It is well established[10] that vulcanization depends on chain reactions initiated by chemical reagents which are radicals in nature, or yield radicals by thermal decomposition or photolytic mechanisms. Farmer and his colleagues have shown[10] that the α-methylenic groups of the rubber chain are the preferential points of attack by free radicals, and they have pointed out the bearing of this fact upon the chemistry of oxidation and polymerization processes. But it has also been demonstrated[11] that disaggregative reactions, such as depolymerizations and mastication in particular, are controlled by free radical mechanisms. Correlation of all these facts appears most plausible if we assume that the formation of chemical bonds between pigment and rubber constitutes an integral part of the chemical crosslinking that may commence during mastication and is completed by vulcanization. All of the interacting partners may be considered to exhibit free radical character at one stage or the other. To test this hypothesis the authors have studied the reactivity of pigment surfaces towards simple organic and inorganic free radicals. A detailed chemistry of carbon surfaces, particularly the significance of chemisorbed oxygen in promoting the free radical character of a carbon surface will be discussed elsewhere[12].

The methods for the preparation of free radicals used in this work consist of:

(1) Thermal decomposition (as related to the cleavage of single bonds).
(2) Step-wise (monovalent) oxidation or reduction.
(3) Polymerization (as related to activation of double bonds and formation of peroxides).
(4) Electrolytic discharge.

The authors have found that any such technique which produced free radicals in the presence of reinforcing or semi-reinforcing fillers gave surface-modified compounds. With multifunctional free radicals the expected crosslinking of filler particles was observed. From the experiments with free radicals they were able to calculate the number of active centers per unit area for a series of filler materials.

EXPERIMENTAL TECHNIQUES AND RESULTS

Thermal decomposition of $S_2O_8^{--}$.—When an aqueous solution of an alkali persulfate is heated above 50° C decomposition sets in; the over-all reaction

$$M_2S_2O_8 + H_2O \rightarrow 2MHSO_4 + O \tag{1}$$

proceeds by the formation of free radical intermediates. The primarily formed SO_4-radical ions can undergo a number of reactions. They can react with hydroxyl ions to give hydroxyl radicals; electron transfer reactions also may take place with some metals of the transition group and a variety of reducing agents. In the presence of olefins covalent bonds may be formed.

TABLE I

DECOMPOSITION OF 0.02 MOLAR PERSULFATE IN THE PRESENCE
OF VARIOUS RUBBER FILLERS

	Moles decomposed after 1 minute	Half lives at 80° C in minutes
Blank	2.89×10^{-4}	99
Silica (A)	3.11×10^{-4}	93
EPC	3.70×10^{-4}	72
MPC	4.07×10^{-4}	63
HMF	4.22×10^{-4}	57
SRF	4.59×10^{-4}	54
MAF	5.14×10^{-4}	45
HAF	5.25×10^{-4}	39

The rate of decomposition of potassium persulfate at 80° C was followed by titration of the sulfuric acid formed with 0.1 N sodium hydroxide. Ten-ml. samples were taken each hour from the reaction batch (5.4062 g. $K_2S_2O_8$ + 400 ml. water) and after titration of the sulfuric acid present the undecomposed persulfate was estimated by separately boiling the solution for 20 minutes and carrying out a second titration. The rate of this decomposition follows very closely a first order mechanism, with $k = 0.425$. The decomposition rates of 0.02 molar potassium persulfate in the presence of 200 sq. m. surface area of various fillers is no longer a first order reaction. Extents of decomposition after one minute, and half-lives of 0.02 molar potassium persulfate are given in Table I. The greatest accelerating effect is shown by the furnace black family; second in order is the group of channel blacks, followed by silica. The products of reaction with persulfate, after being freed from electrolyte by repeated washing on a centrifuge with alcohol-water mixtures, showed very remarkable changes in dispersibility. HAF black, even after prolonged drying, dispersed easily in water with the formation of a stable colloidal suspension (*q.v.* Figure 1). EPC black, after identical treatment, lost its ability to form colloidal suspensions on drying. To show that this phenomenon was not due to ionic adsorption of SO_4^{--}, the same blacks were similarly treated with 0.02 molar solution of potassium sulfate and sulfuric acid. Carbons so treated could be washed free of electrolyte and showed no tendency to disperse colloidally.
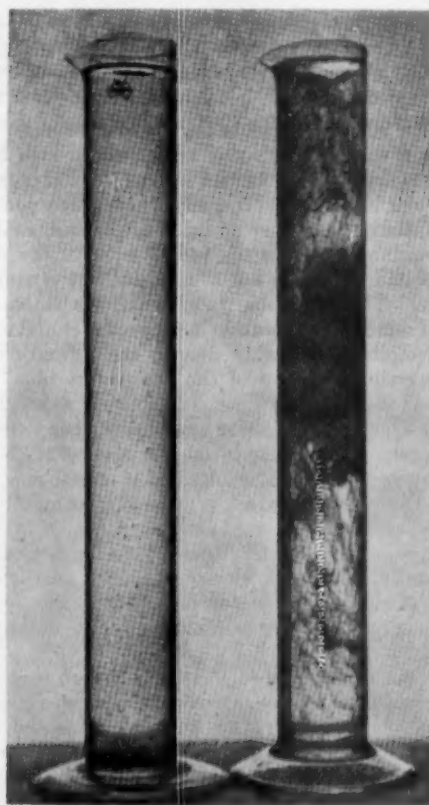
Fig. 1.—Carbon in the process of dispersion in water after persulfate treatment.
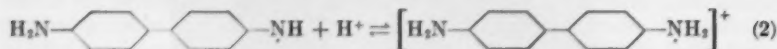(Original carbon on left.)

Stepwise oxidation of benzidine.—Organic oxidation-reduction systems are generally bivalent and the radical is intermediate between the oxidized and reduced state of a substance. Some of them, particularly those stabilized by resonance, are deeply colored, e.g., the cation formed from benzidine by mono-

TABLE II

Some Characteristic Properties of Various Rubber Fillers[*]

Filler	Formula	Average particle diam. (mμ)	Density	pH	Specific surface m.²/g.	Active centers /100 sq. Å
Chemically treated halloysite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	0.065	2.35	8.0	39	3.1
Furnace black	HAF type	0.038	1.80	8.8	81	2.3
Channel black	EPC type	0.030	1.80	4.3	106	1.2
Channel black	HPC type	0.025	1.77	4.1–4.5	125	0.9
Silica (A)	$SiO_2 \cdot nH_2O$	0.025	1.95	8.0–9.0	123	0.08–0.09
Silica (G)	$SiO_2 \cdot nH_2O$	0.014	2.2	4.5	109–182	0.02–0.03
Calcium silicate	$CaO \cdot SiO_2 \cdot nH_2O$	0.030	2.1	9.8–10.2	66	0.01–0.02

[*] The figures for particle size, density, and pH are generally those supplied by manufacturers, with the exception of the particle size of the halloysite, which was taken from the article by Flemmer[6].

valent oxidation with permanganate[12] in acid solution

$$H_2N\!-\!\bigcirc\!-\!\bigcirc\!-\!\overset{.}{N}H + H^+ \rightleftharpoons \left[H_2N\!-\!\bigcirc\!-\!\bigcirc\!-\!\overset{.}{N}H_2\right]^+ \quad (2)$$

For our tests with the rubber pigments the "benzidine blue" reagent was prepared by saturating a 0.5 per cent acetic acid solution with benzidine at room temperature. On stepwise oxidation with approx. $N/200$ potassium permanganate a deep blue color is developed initially which corresponds to the cationic semiquinone shown above. Further addition of permanganate solution causes oxidation of both amino groups in the molecule, with the development of a stable yellow compound, which is not a diradical but is stabilized through a quinonoid structure. The deep blue intermediate is stable only for a brief period; after several minutes the solution becomes violet and eventually forms a dark, flocculent precipitate, probably due to the formation of dimerization products. An irreversible reaction of the "benzidine blue" compound with the filler surfaces was studied over a range of concentrations by shaking vigorously 0.5 to 5.0 g. of filler with increasing amounts of "benzidine blue" solutions. After rapid centrifuging, it was judged from the color of the supernatant liquid when maximum uptake of the blue compound was reached. The results obtained are given in Table II from which it appears that no direct relation exists between particle size and the number of active centers per unit area. Furthermore, greater activity is exhibited by furnace type black than by channel type black. This is again in agreement with our findings on the effects of various fillers on the rate of decomposition of persulfate. The significance of the extraordinarily high number of active centers of the halloysite sample will be discussed later.

To demonstrate the mechanism of chemisorption on carbon surfaces of the monooxidation product of benzidine, a carbon sample was treated with the requisite amount of this material and, after washing, subjected to further oxidation. If the oxidation proceeds stepwise leading to chemisorption of a radical through one oxidized amino group, further oxidation of the product stabilized on the carbon surface should lead to a certain amount of crosslinking through the oxidation of the remaining amino group. As the material is difficult to centrifuge after the first stage of oxidation, it appears that disaggregation of the carbon agglomerates initially present has taken place during this step. On further oxidation of the isolated and washed material under similar conditions, the particles settle immediately, indicating some crosslinking.

Kolbe reaction with a carbon electrode.—Preliminary experiments had shown that decomposition of benzoyl peroxide in toluene in the presence of a reinforcing carbon black resulted in changed dispersion characteristics of the black, probably due to the attachment of $C_6H_5C\!-\!O\cdot$ or $\cdot C_6H_5$ free radicals to the

$$\overset{\|}{O}$$

carbon surface. The effect, however, as was to be expected, was not very great. It was therefore decided to produce stearate free radicals by the Kolbe reaction. Although the simple ionic discharge and dimerization theory is inadequate to account for the great variety of products formed, Waters[14] pointed out that all features of the Kolbe reaction can be explained as reactions of the primary formation of carboxylate free radicals. A carbon electrode was formed by sucking 20 g. of a reinforcing black on to a glass sinter plate of approximately 50 sq. cm. surface, to be used as the anode in electrolyzing a 1 per cent aqueous

solution of potassium stearate at room temperature.   A potential of 3 volts was applied for 120 hours.   After this period of time the carbon was washed free of electrolyte and byproducts (such as hydrocarbons) using water, alcohol, and carbon tetrachloride as the washing liquors.   The dried carbon easily floated on water.   When, however, the same original carbon was shaken with 1 per cent potassium stearate solution for 24 hours, potassium stearate could be washed out completely leaving unaltered carbon, which sank in water.   Experiments to determine a contact angle by discharging stearate ions on a smooth carbon surface failed, since attempts to wash off the white layer formed after a few minutes of electrolysis damaged the smooth surface.

Styrene-carbon gel formation.—The conception of a free radical (electron-pairing) mechanism as the basis of a chemical interaction of filler and rubber matrix was further tested with systems where diradicals or multifunctional radicals are known to be formed.   Under these conditions crosslinking and gel
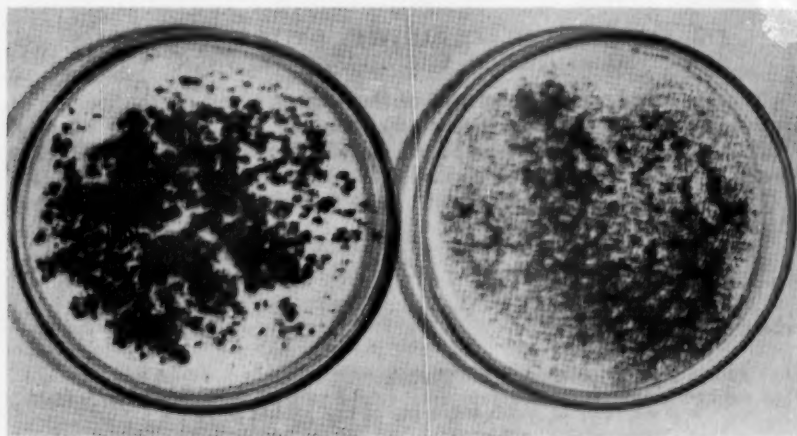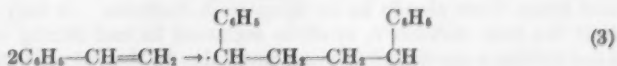

Fig. 2.—Carbon-polystrene gel compared with original carbon.

formation may be expected to occur.   Since the process of initiation in un-catalyzed mass-polymerization of styrene is second order with respect to the monomer, it has been suggested that initiation involves dimerization of the monomer:

$$2C_6H_5-CH=CH_2 \rightarrow \cdot \underset{\overset{|}{C_6H_5}}{CH}-CH_2-CH_2-\underset{\overset{|}{C_6H_5}}{CH} \tag{3}$$

Freshly prepared styrene monomer was polymerized over a range of temperatures from 30–100° C.   Reinforcing carbon black was added at different stages of the polymerization, but in no instance could gel formation be observed.   The interaction of oxygen with styrene is known to result in the production of peroxides[15], which may generate free radicals as a result of their thermal instability.   Oxygen is also known to promote the formation of branched chains[16], although the exact mechanism of this reaction is still obscure.   Styrene monomer was allowed to absorb various amounts of oxygen prior to polymerization. At 0° C styrene monomer absorbed 14 times its volume of oxygen in 4 days and

appeared not visibly increased in viscosity. A portion of this sample was placed under nitrogen at 30° C. Polymerization started within a few days. When polymerization had proceeded to approximately 20 per cent, HAF black was added and produced spontaneous gelation, resulting in one single agglomerate whose individual components could not be separated by solvent extraction. Analysis showed that the gel had a composition of 44.6 per cent styrene and 55.4 per cent carbon black. Similarly, styrene monomer was treated with dry oxygen at 40° C until it had absorbed six times its volume and allowed to polymerize under nitrogen at 70° C. The gel produced is shown in Figure 2; it contained 34.6 per cent styrene. It is considered to represent a stage reached in the development of polyfunctional free radicals which are necessary for crosslinking. In no instance was gelation observed when polystyrene granules were dissolved in a solvent and carbon black added. The formation of styrene-carbon gels in this manner is believed to represent a close analogue to the formation of carbon-gel with rubber.

THE EFFECT OF FILLER ACTIVITY ON THE STATISTICAL MECHANICS OF THE RUBBER NETWORK

The statistical treatment of rubber elasticity is based on the method of statistical mechanics of the network as applied by Kuhn[17]. More recently, Wall[18] and Treloar[19] computed the elastic retractive force from the entropy change in passing from the undeformed to the deformed state. For the tension τ (force per unit initial cross-sectional area) the following equation was thus obtained:

$$\tau = kT \frac{\nu}{V} \phi(\alpha) \tag{4}$$

where $\phi(\alpha) = \alpha - \dfrac{1}{\alpha^2}$

V = total volume of the system

ν = number of chain segments of the rubber network.

The above theory formed the basis for stress-strain analysis of unfilled rubber by making assumptions on the distribution of molecular length. The number of chain segments produced by vulcanization may be considered constant for any particular rubber under definite conditions of cure. Considering that an active filler forms additional chain segments by reaction with rubber, the additional number of segments should be related to the number of active sites and hence there should be an increase in modulus. It may thus be assumed that the total number ν, of chain segments formed during vulcanization of a filled rubber is composed of ν_1 segments due to the vulcanization process and ν_2 segments resulting from rubber-filler interaction. For constant conditions of vulcanization at constant volume loadings of the various fillers, the modulus therefore will depend on ν_2.

Thus Equation (4) becomes

$$\tau = kT \left(\frac{\nu_1 + \nu_2}{V} \right) \phi(\alpha) \tag{5}$$

The number of chain segments due to rubber-filler interaction (ν_2) may be deduced from the total number of active sites on the filler surface (n) by a statisti-

cal treatment. Let there be N polymer chains, and let N_i represent the number of chains carrying i-active points. Then

$$\nu_2 = n - N + N_0 \tag{6}$$

if one considers that only those polymer chains will contribute to modulus which have at least two points of attachment. The number of different arrangements of n active sites over N polymer chains such that there are N_0 chains with no active sites, N_1 chains with one active site, N_2 with two active sites, etc., is given by

$$P = \frac{N!}{\prod_i N_i!} \tag{7}$$

Hence, for the most probable distribution, it follows that

$$\nu_2 \simeq n - N + \frac{N}{1 + \dfrac{n}{N}} \tag{8}$$

and for filler loadings of practical interest (very large values of n), the equation becomes

$$\nu_2 = n - N \tag{9}$$

Thus, for the tension τ we obtain

$$\tau = kT \left(\frac{\nu_1 + n - N}{V} \right) \phi(\alpha) \tag{10}$$

Let σ be the number of active sites per unit area of filler surface, ν_1 and ν_2 the volume fractions of polymer and filler respectively, then the total number (n) of active sites becomes

$$n = \frac{3\sigma}{r} \, \nu_2 \cdot V \tag{11}$$

where r = particle radius. Further

$$N = \frac{\nu_1 \cdot V \cdot \rho}{m} \tag{12}$$

where ρ is the density of the polymer and m the mass of one polymer chain. Hence

$$\frac{\tau}{\phi(\alpha)} = kT \left[3\nu_2 \cdot \frac{\sigma}{r} - \nu_1 \frac{\rho}{m} + \frac{\nu_1}{V} \right] \tag{13}$$

Therefore, for constant volume loadings of the different fillers under constant conditions of cure, the modulus (for small elongations) should be controlled by the term σ/r.

Rubber tests were carried out with a number of carbon blacks and white fillers of known particle size and for which σ had been obtained by experiments

with free radicals as shown earlier.   The formulation used was:—

Masticated smoked sheet	100
Stearic acid	4
Zinc oxide	5
Mercaptobenzothiazole	1
Sulfur	3
Agerite white	1.5
Filler	25 volumes
Temperature	160° C

Test results as given in Table III indicate that in almost all cases optimum vulcanization is reached after approximately 10 minutes.   At shorter periods no full use is made of the active sites introduced by the fillers, whereas at 15 minutes, some overvulcanization becomes apparent.   The evaluation of results therefore was confined to figures for a 10-minute rubber.   The group of properties which may reasonably be expected to be controlled by the network structure are modulus, resilience, and hardness.   These properties are determined by nondestructive tests, while tensile strength, elongation at break, tear resistance, and abrasion involve destruction of rubber-sulfur and rubber-carbon bonds. Theory, as set out in the foregoing, should strictly hold only for extensions of filler-loaded rubber up to approximately 40 to 50 per cent elongation, where a linear stress-strain relationship exists.   It is a fortunate fact, however, that for filler-loaded rubber (particularly for carbon-black loaded material) the stress-strain function, after deviating from linearity for elongations above 40 to 50 per cent, changes its character again at elongations of approx. 200 per cent, and in the vicinity of 250 to 300 per cent once more reaches the line obtained by linear extension of the first part of the stress-strain curve.

Figure 3 shows the linear relation between the modulus (after a 10-minute vulcanization) and σ/r, as required by Equation (13).   Since modulus is considered to be the main contributing factor towards hardness and resilience, a similar simple relation should exist between these properties and σ/r.   This conception is borne out to some extent by the results represented in Figure 4.

It will be noted that the halloysite used in the experiments does not conform with the statistical treatment of network formation as set out above.   The particular halloysite, of the general formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ contained also a high proportion of organic acids neutralized by organic and mineral bases. This organic part is said to be paramount in developing reinforcing properties, but temperatures as low as 60° C cause decomposition, as evidenced by evolution of amine vapors.   At higher vulcanization temperatures only part of the active sites, as represented by the experimental value of σ, remain available for crosslinking.

It has been suggested that the main difference between furnace blacks and channel blacks is to be found in the high structure[20] (chain formation) of the former.   The active sites of channel blacks are not available for chain formation because of the masking effects of the adsorbed gases; mixing causes desorption of these gases producing the active areas necessary for reinforcement.   In furnace blacks, however, the active sites cause formation of chains which break down on milling.   From our experiments, in which furnace blacks were found to be intrinsically more active towards free radicals than channel blacks, it would appear that this chain formation is due to the same mechanism, namely, the pairing of single electrons.   Thus it is felt that scorching difficulties found with furnace blacks most likely also reflect the high activity of these blacks. Although the view is held[21] that high structure blacks generally give vulcani-

TABLE III

Filler	e/r	Cure, min.	Ultimate tensile strength, lb./s. in.³		Per cent elongation at break		Modulus at 300%, lb./sq. in.²		Tear resistance, lb./in.³	% resilience	Shore hardness		Abrasion resistance, % vol. loss compared with standard
			Normal	Aged	Normal	Aged	Normal	Aged			Normal	Aged	
HAF	121	5	2790	3170	440	430	1520	2060	580	56	57	62	115[1]
		10	2820	2870	410	340	1840	2440	750	55	63	65	
		15	2800	2440	400	320	1880	2300	540	54	63	66	
EPC	80	5	2180	3180	560	555	720	1200	380	57	48	53	85[1]
		10	3360	3230	530	470	1370	1830	780	58	57	63	
		15	3000	2940	500	420	1280	1870	670	57	60	66	
HPC	69	5	2590	3120	570	540	740	1180	310	60	47	55	80[1]
		10	3360	3230	540	490	1230	1630	820	61	54	60	
		15	3030	2630	490	420	1230	1650	600	60	57	65	
Silica	4.3	5	2680	2800	640	590	500	820	450	62	45	51	130[2]
		10	2570	2760	660	590	495	780	330	62	50	53	
		15	2380	2690	670	620	430	690	270	59	50	52	
Calcium silicate	1	5	2350	2480	660	630	440	540	260	64	46	47	240[2]
		10	2200	2000	650	610	440	510	270	64	48	48	
		15	2200	1990	650	610	450	510	250	64	48	48	
Halloysite	94	5	3340	2930	540	460	1110	1610	280	77	55	61	150[2]
		10	2860	2450	520	430	1090	1520	180	76	55	61	
		15	2700	2420	510	430	990	1390	140	76	53	60	

[1] Vulcanized 12 minutes.
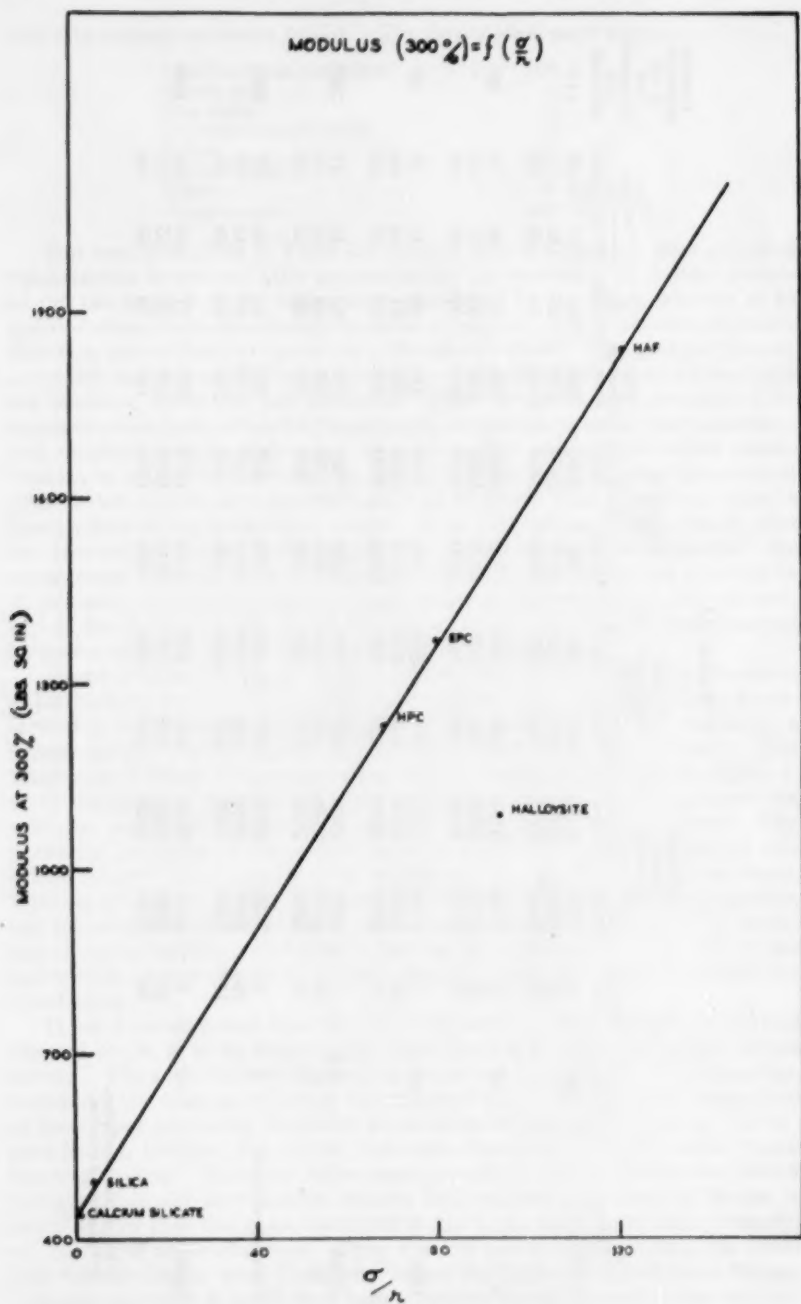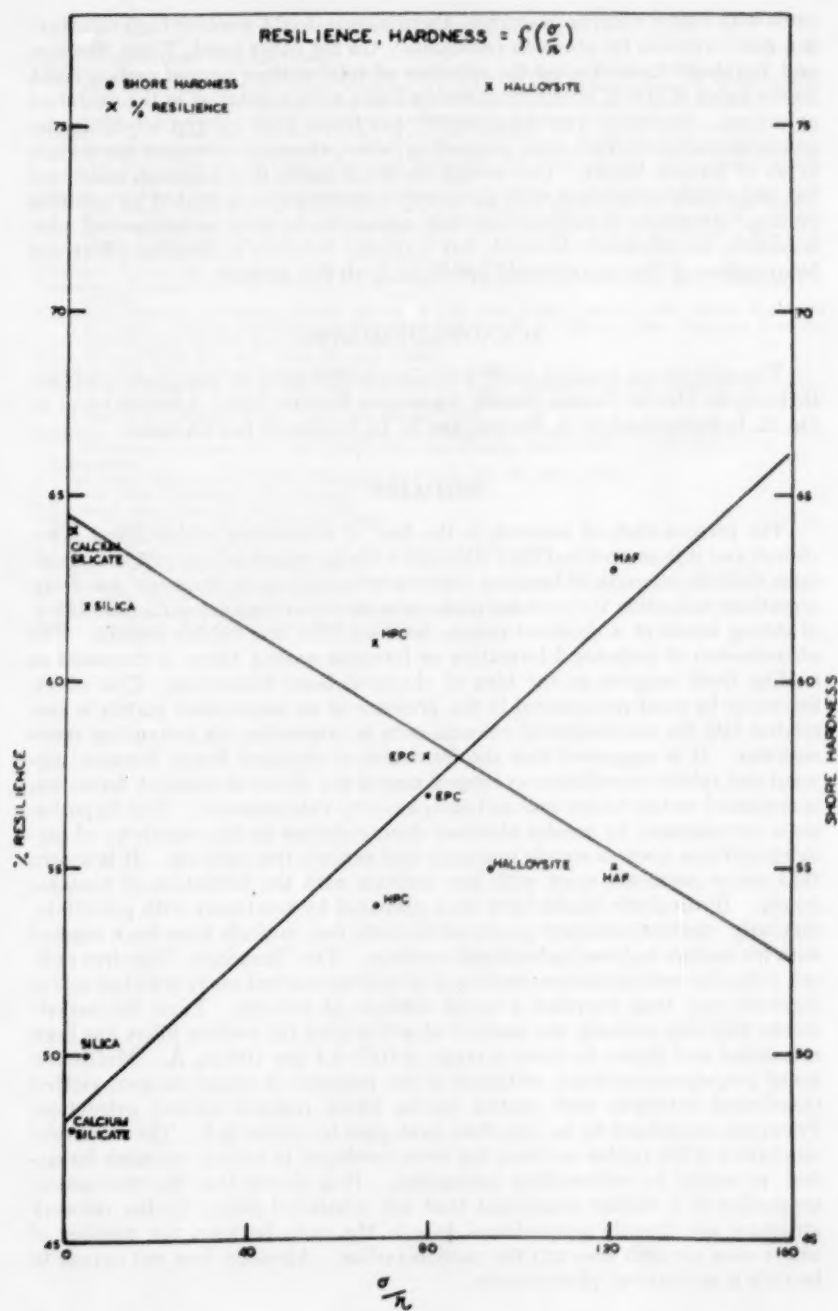[2] Vulcanized 8 minutes.

Fig. 3.

FIG. 4.

zates with better wearing properties, there is some doubt whether high structure is a good criterion for abrasion resistance. On the other hand, Winn, Shelton, and Turnbull[22] have studied the influence of total surface area of carbon black on the aging of GR-S, considering carbon black to be a catalyst in the oxidation of rubber. Similarly, van Amerongen[23] has found that oxygen solubility depends on carbon surface area, suggesting better abrasion resistance for certain types of furnace blacks. Our results do not indicate that abrasion resistance has any simple connection with the network structure as indicated by modulus values. Abrasion, therefore, does not appear to be only a mechanical phenomenon, as commonly thought, but probably involves a chemical effect due to oxidation of the continuously produced fresh tire surface.

ACKNOWLEDGMENTS

SUMMARY

The present state of research in the field of reinforcing rubber fillers is reviewed and it is pointed out that although a strong school of thought still maintains that the strength of bonding depends on particle size, there are many observations indicating the presence of reactive sites and suggesting the possibility of strong bonds of a chemical nature between filler and rubber matrix. The phenomenon of carbon-gel formation as foremost among these, is discussed as lending fresh support to the idea of chemical bond formation. This effect, known to be most pronounced in the presence of an *unsaturated* matrix is correlated with the mechanism of vulcanization as proceeding via *free radical intermediates*. It is suggested that the formation of chemical bonds between pigment and rubber constitutes an *integral part* of the chemical crosslink formation commenced on the rubber mill and completed by vulcanization. This hypothesis is corroborated by results obtained during studies on the reactivity of pigment surfaces towards simple inorganic and organic free radicals. It is shown that active pigments react with free radicals with the formation of nonionic bonds. Hydrophilic blacks have been prepared by treatment with persulfate. Similarly, electrochemically produced stearate free radicals have been reacted with the surface to form hydrophobic carbons. The "benzidine "blue free radical, being the monooxidation product of benzidine, reacted easily with less active pigments and thus provided a useful measure of activity. From the experiments with free radicals, the number of active sites for various fillers has been calculated and shown to cover a range of 0.01–3.1 per 100 sq. Å. Multifunctional polystyrene radicals, obtained in the presence of excess oxygen, yielded crosslinked networks with carbon blacks which resisted solvent extraction. These are considered to be complete analogues to carbon gel. The statistical mechanics of the rubber network has been developed to include crosslink formation as caused by rubber-filler interaction. It is shown that the mechanical properties of a rubber compound that are controlled solely by the network structure are directly proportional to σ/r, the ratio between the number of active sites per unit area and the particle radius. Abrasion does not appear to be only a mechanical phenomenon.

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BEHAVIOR OF HIGHLY-FILLED RUBBER VULCANIZATES *

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INTRODUCTION

It is well known that physical properties such as tensile strength, tear resistance, and abrasion resistance of a filled vulcanizate pass through an optimum as the percentage of mineral or carbon filler increases. The behavior of very highly filled vulcanizates containing 40 to 60 per cent filler by volume has been comparatively little studied, since physical properties are then well past the optimum, and deteriorating as the filler content increases. The present investigation was undertaken to determine the point at which these highly-filled materials lose their extensibility, becoming brittle, and the factors which govern this.

Very little reference is made to carbon black stocks since mixes at relatively low volume percentages are too stiff for manipulation on a mill, or for molding.

EXPERIMENTAL

Recipes.—The following recipes and curing times were generally used, unless specific effects were being sought:

Filler	x	Filler	x
Pale crepe	100	GR-8 (Polysar 8)	100
Zinc oxide	5	Zinc oxide	5
Stearic acid	1	Stearic acid	1
Sulfur	3	Mercaptobenzothiazole	1
Mercaptobenzothiazole	1	Diphenylguanidine	0.5
		Sulfur	3
Cure 30 min. at 141.5° C		Cure 40 min. at 145° C	

Filler	x	Filler	x
Butadiene acrylonitrile		Butyl rubber (Polysar Butyl)	100
rubber (Hycar OR-15)	100	Zinc oxide	5
Zinc oxide	5	Stearic acid	1
Stearic acid	1	Sulfur	1.6
Diphenylguanidine	0.1	Tetramethylthiuram disulfide	1
N-Cyclohexyl benzothiazole-		Mercaptobenzothiazole	1
2-sulfenamide	1		
Sulfur	2.5		
Cure 40 min. at 145° C		Cure 45 min. at 150° C	

Since the density of the fillers varied widely, results are always compared on a volume/volume basis.

Stress-strain curves.—These were normally measured on a Goodbrand R5 tensile testing machine, using rings cut from 4 mm. molded sheet with an elongation rate of 5 inches/minute, corresponding to about 160 per cent/minute.

For measurements at low elongations a BRPRA modulus tester[1] was used, with molded dumbbell specimens of effective length 15 cm. Extensions were carried out stepwise at 10 per cent intervals with the same timing as for the volume change measurements.

Volume changes on elongation.—The apparatus used was essentially the same as that of Holt and McPherson[2], the tube being made of glass with a sealed-on side tube, graduated Veridia glass capillaries, and brass end plugs. The specimen was that used with the BRPRA modulus tester, the grips
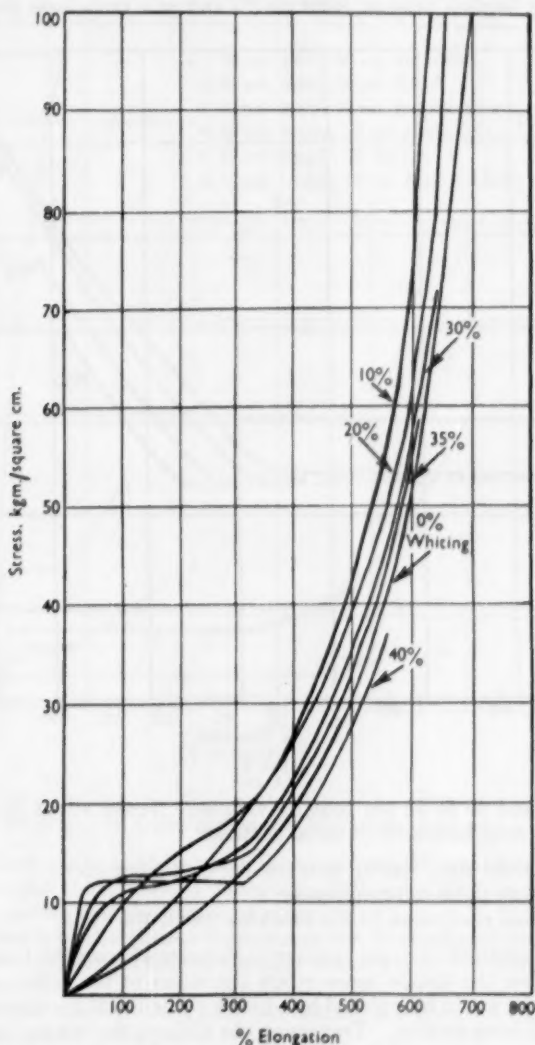
Fig. 1.

being modified accordingly, this giving a relatively higher specimen volume to give easily readable volume changes over the limited elongation range of 0–100 per cent.   The apparatus was immersed in a large thermostatted tank, the practicable size of which limited the elongation which could be used with the available specimen.

EXPERIMENTAL RESULTS

Stress-strain curves.—Figures 1 and 2 show the stress-strain curves obtained with whiting (surface area ca. 8000 cm.$^{-1}$) and pale crepe over the ranges 0 to
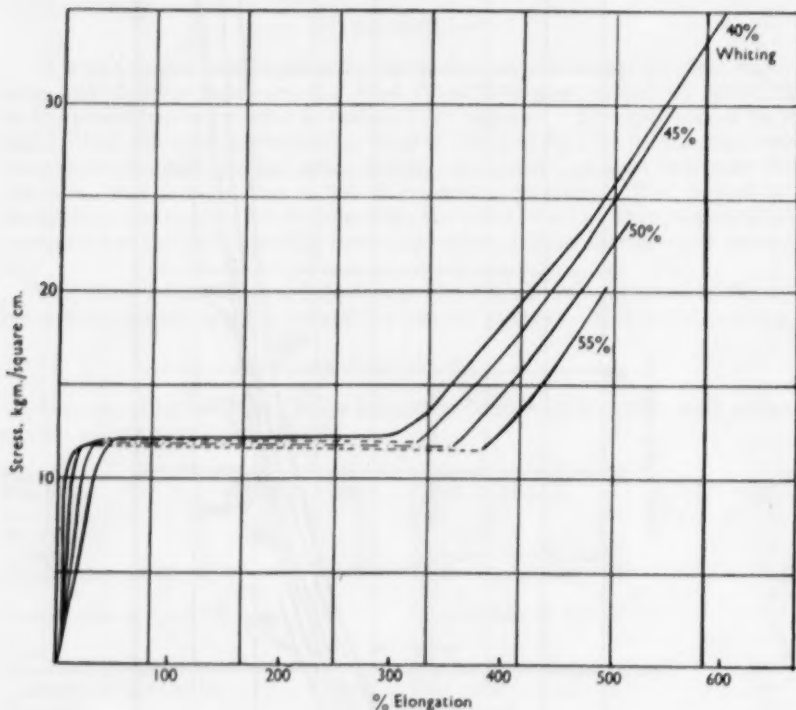
Fig. 2.

40 per cent and 40 to 55 per cent by volume.   Above about 35 per cent the curve can be seen to consist of three portions:

    (a) the initial steep rise up to a few per cent elongation;
    (b) the plateau at constant stress;
    (c) the final elongation to the breaking point, the "tail."

On the plateau the sample appears to elongate at constant tension, but this is only because the tensile tester refers the stress to the initial cross-section, and the plateau would be replaced by a gently rising line if the stress was referred to the actual cross-section.   Traversing the plateau the sample frequently has a knotted appearance with hard lumps separated by softer material until at

the end of the plateau, the knots have disappeared. Considerable permanent set is obtained, and a second elongation gives a curve resembling in shape that of a gum stock.

This plateau effect has been found for a number of mineral fillers with several rubbers, e.g., whiting, barium sulfate, sodium sulfate, sodium carbonate, and clay with pale crepe, GR-S, Hycar OR-15, and Butyl rubber (see Figure 3). It is therefore to be regarded as a general effect and not confined to any given elastomer/filler system, though it may not always be observed.

1. 50 vol. $BaSO_4$ 50 vol. Hycar OR.
2. 50 vol. $BaSO_4$ 50 vol. GR - S.
3. 50 vol. $BaSO_4$ 50 vol. Butyl Rubber.
4. 50 vol. Na_2SO_4 50 vol. Hycar OR.
5. 50 vol. Na_2SO_4 50 vol. GR - S.
6. 50 vol. Na_2SO_4 50 vol. Butyl Rubber
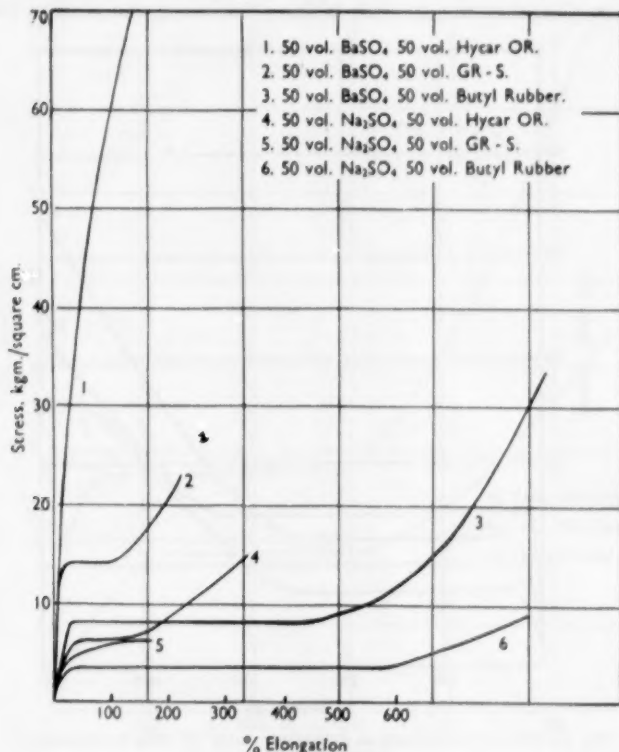
FIG. 3.

The chief properties of these curves can be summarized as:

(a) The slope of the initial portion increases with filler content.
(b) The height of the plateau varies very little with the filler content for a given system and the degree of cure.
(c) The length of the plateau increases as the filler content increases.
(d) The tensile strength falls as the filler content rises, i.e., the tail becomes shorter.
(e) As the particle size of the filler is increased at a given loading the height of the plateau is reduced.
(f) As the modulus of the base stock is increased, the plateau rises.

As the filler content is progressively increased the tensile strength will eventually fall to a value equivalent to the height of the plateau, and the elongation at break becomes indeterminate, the vulcanizate then being about to become brittle.

The suggested interpretation of these curves is as follows:

Over the steep initial portion of the curve the sample is stretching largely as a whole, the filler particles being stuck to the rubber. At some stress the rubber begins to pull away from the filler particles ("dewetting") and the softened rubber elongates, this process taking place along the plateau until the
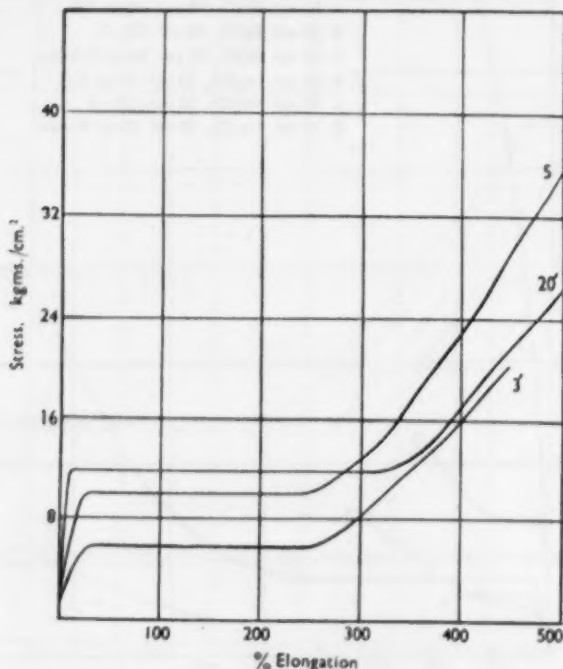
Fig. 4.—Effect of time of cure on stress-strain curve. Whiting in pale crepe.

system resembles sponge rubber, with filler particles lying in the holes, but not adhering to the rubber. The plateau ends when the elongation of the sponge-like matrix is such that the same load as applied at the beginning of the plateau will produce no further elongation in the dewetted rubber. The tail then represents the further elongation of the sponge under increasing load until it finally breaks.

The increase in the initial slope with the filler content is the usual stiffening effect of fillers. It is reasonable to suppose that the stress at which the rubber-filler bonds break is independent of the filler content for a given system, and hence the height of the beginning of the plateau is fixed. The more filler is present, the more tenuous is the sponge after dewetting and so the higher the elongation corresponding to a given load, i.e., the lower is the modulus after

dewetting. Similarly, the less rubber, the lower is the tensile strength of the sponge. The case of natural rubber is slightly different from that of the butadiene copolymer synthetics in that crystallization can take place in the tail.

The modulus of the base stock can be varied by altering the time of cure, and it is found that increasing the time of cure raises the plateau (Figure 4). Similarly, the height of the plateau is reduced by inclusion of softeners such as Cycline Oil or dibutyl phthalate (Figure 5), but the lowering of the tensile
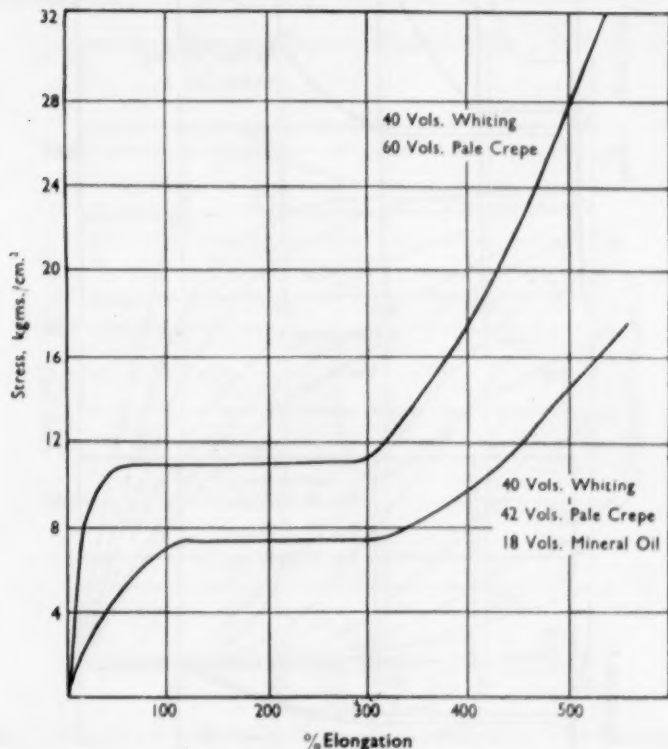
Fig. 5.

strength, in absolute units, is always greater than the lowering of the plateau. Consequently, a softened base stock will accept less filler before becoming brittle after curing than the original unsoftened material. Again, increasing the modulus by the incorporation of carbon black, or by using rubber obtained from a latex in which methyl methacrylate had been polymerized, raises the plateau, and in addition with synthetics such as GR-S and Hycar OR-15, the height of the plateau and also the length of the tail can be increased by the addition of carbon black or methyl methacrylate (as above, Figure 6) so that more noncarbon filler can be incorporated before brittleness is reached, though this is limited by the stiffness of the mix on the mixing rolls. With whiting and
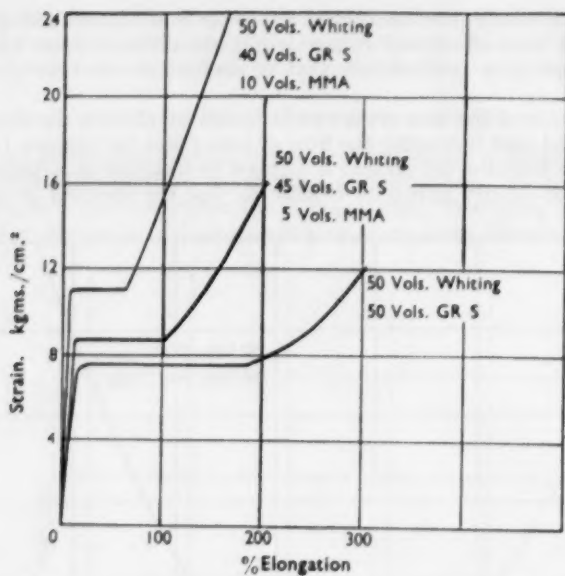
FIG. 6.
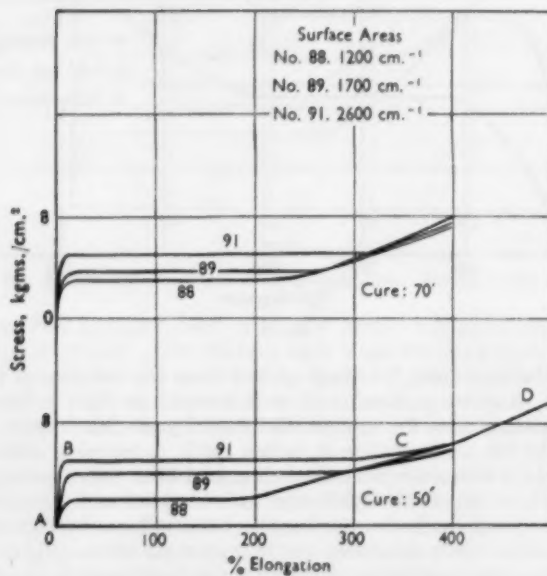
FIG. 7.—Effect of particle size on stress-strain curve.

pale crepe it was found that of the wetting agents investigated, only cetyl pyridinium bromide had any definite effect, raising and shortening the plateau, and increasing the tensile strength.

Decreasing the particle size of the filler increases the load at which the plateau appears (Figure 7), though in the range 10 to 15 mμ the effect is less marked than that of modulus. As shown below, this indicates, in conformity with the observations of Jones and Yiengst[3], that at a given elongation a higher fraction of large particles is dewetted than small ones. Thus at a given elongation, when approaching the plateau, and dewetting has commenced, the modulus of a
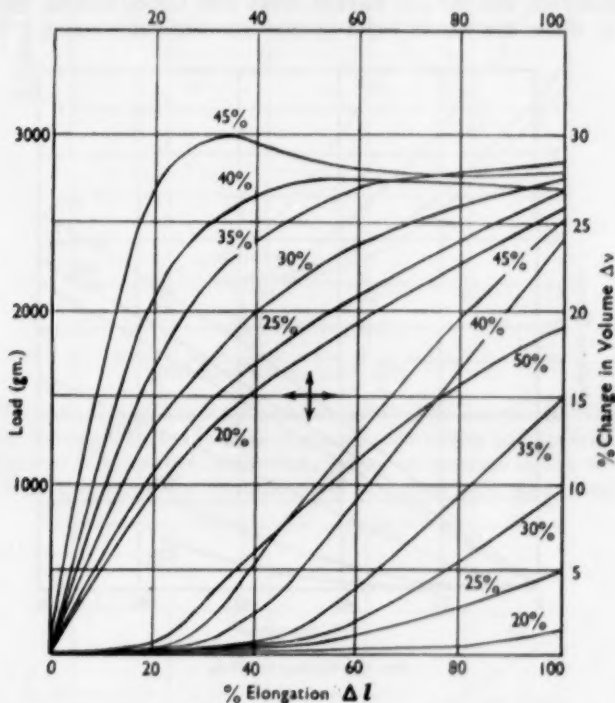
Fig. 8.—Comparison of stress-strain and $\Delta\nu$-strain curves for whiting-pale crepe vulcanizates.

small particle mix will be higher than that of a large particle mix. The modulus effect then raises the height of the plateau.

If the particle size is very small, as in the case of reinforcing carbon blacks, the plateau may not be observed, though a practical limit is set here by the stiffness of the mix on the mixing mill.

Volume changes on elongation.—In general, the findings of Jones and Yiengst[3] were confirmed, as extended to the systems whiting/pale crepe and whiting/GR-S, that increasing filler content led to an increased volume change ($\Delta\nu$) for a given elongation (Δl), and that small particles gave a smaller $\Delta\nu$ than large ones. In Figure 8 the $\Delta\nu/\Delta l$ curves and the stress-strain curves (measured on the BRPRA modulus tester) are compared, and it is seen that the beginning of the plateau corresponds to the onset of the steeper part of the

$\Delta\nu/\Delta l$ curve. It was also confirmed that when the stock was undercured the $\Delta\nu/\Delta l$ curve lay below that of a rubber cured to optimum modulus, over the range tested. This is due to the modulus of the rubber, since a small amount of carbon black or the addition, at low filler concentrations, of a wetting agent which increases the modulus of the specimen, produce an opposite effect to an undercure.

This observed effect of modulus will also explain qualitatively why, with pale crepe/whiting vulcanizates, the 50 per cent by volume $\Delta\nu/\Delta l$ curve crosses the 45 and 40 per cent curves at elongations above about 50 per cent and 75 per cent respectively, and the less marked effect with GR-S/whiting vulcanizates (Figure 9) where the curves begin to converge without crossing. When de-
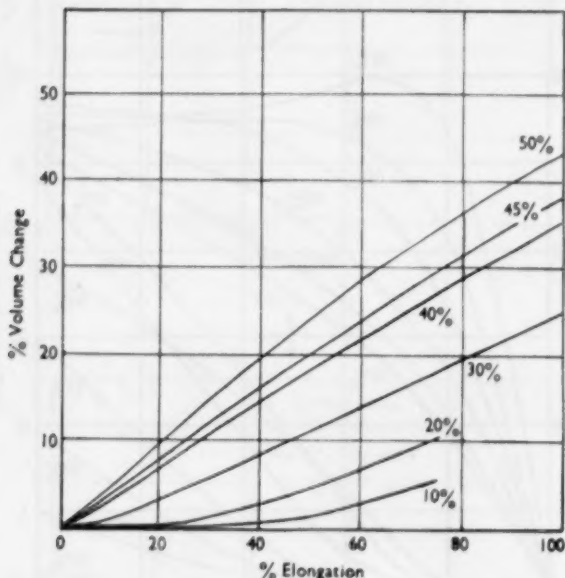
Fig. 9.—Whiting in GR-S.

wetting takes place along the plateau, the knots observed in the specimen correspond to undewetted portions of high modulus several times that of the gum stock network, which approximates to that of the dewetted portions. Hence, as the specimen is elongated there are two opposing effects, firstly the increase in volume due to increased dewetting, and secondly the decrease in volume due to the change in modulus. As the elongation increases the relative proportion of dewetted material increases, and so the $\Delta\nu/\Delta l$ curve bends over, the second effect finally predominating. The difference between the pale crepe and GR-S curves presumably arises from the higher modulus of the GR-S stocks at low elongations compared with pale crepe.

The finding of Jones and Yiengst that small particles gave smaller $\Delta\nu$ at a given elongation and loading is confirmed by this work. The effects of particle size and modulus explain the effects of wetting agent in the whiting/pale crepe system where at low filler loadings (25 per cent by volume), $\Delta\nu$ is increased
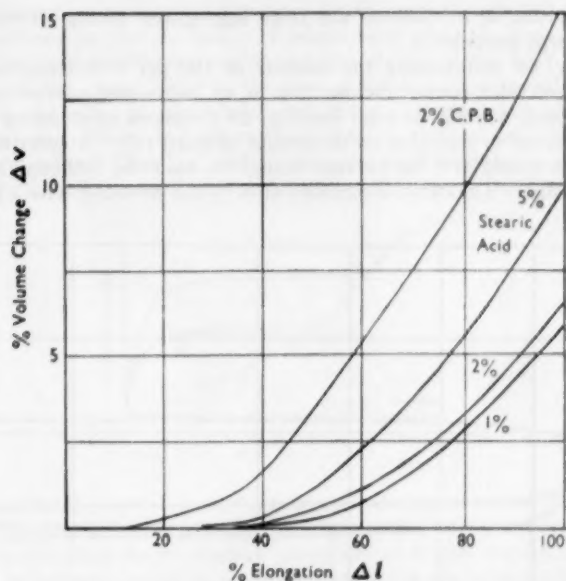
FIG. 10.—Effect of wetting agent at low (25 per cent by volume) filler content (whiting/pale crepe).

(Figure 10), and at high loadings (50 per cent) it is decreased (Figure 11). At low filler loadings the modulus is increased, due either to improved dispersion or increased filler rubber interaction, giving an increase in $\Delta\nu$, whereas at high filler loadings, where the dispersion will be poorer with many large aggre-
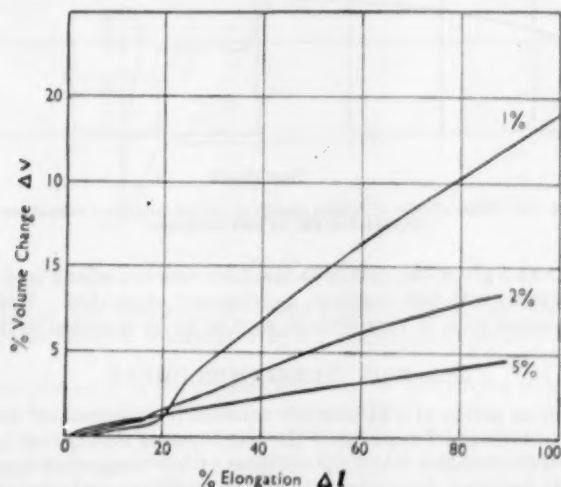

FIG. 11.—Effect of stearic acid at high (50 per cent by volume) filler content (whiting/pale crepe).

gates, the action is to disperse the large aggregates, giving effectively small instead of large particles.

Similarly, on maintaining the rubbers at 100 per cent elongation, $\Delta\nu$ increases at low filler concentrations due to an increasing number of particles being dewetted, whereas at high loadings $\Delta\nu$ decreases on standing because of the large change in modulus on dewetting (Figure 12). A suitable choice of filler content would give no volume change on standing although the tension drops markedly. The effect of repeated slow cyclic stressing, which leads to an
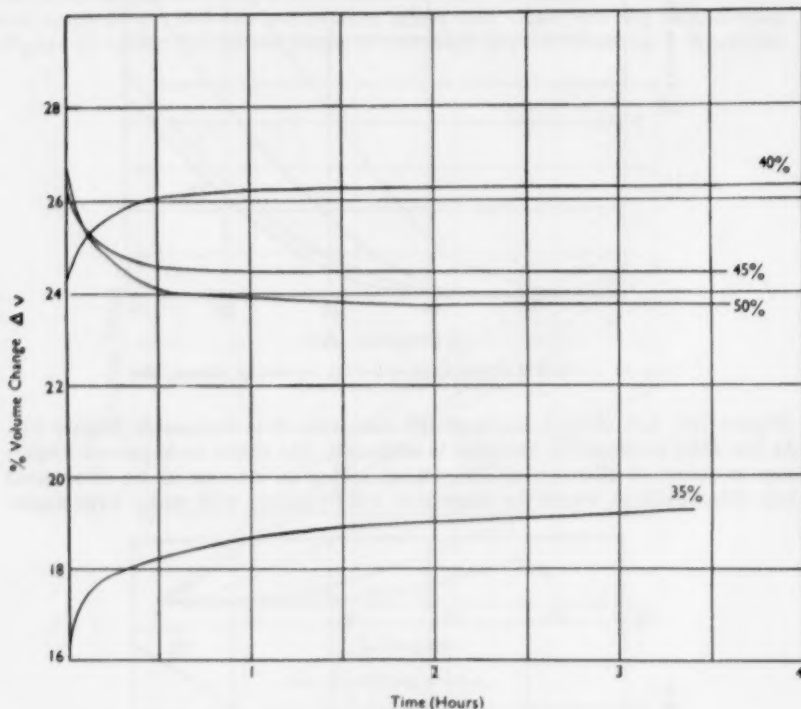
Fig. 12.—Effect of time on volume change of whiting/pale crepe vulcanizate maintained at 100 per cent elongation.

increase in $\Delta\nu$ at a given elongation at low filler concentrations, and a decrease after the first cycle with high loadings, are similarly explicable. With whiting/GR-S vulcanizates there is very little change in $\Delta\nu$ on repeated cycling.

RELATION TO REINFORCEMENT

The stiffening action of a filler is not necessarily accompanied by reinforcement in the technological sense since the latter passes through an optimum as the filler content increases while the stiffness at low elongation increases continuously. It has been demonstrated with many fillers, and particularly with carbon black, that the reinforcing action increases, at a given loading, as the

particle size decreases, when good dispersion is attained, though bad dispersion appears sometimes to obscure this. It seems very probable that there is a relationship between reinforcing action and the ability of the filler to remain stuck to the rubber, particularly in the case of the butadiene-copolymer synthetic rubbers where the physical properties of the gum stock are very inferior to those of natural rubber, and where there is no crystallization. The results presented here indicate that low particle size and high modulus contribute to reduce dewetting, and the small reinforcing action of fillers on Butyl rubber may
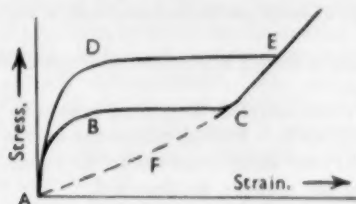
Fig. 13.

possibly be due to the very low modulus of the gum stock at low elongations, compared with natural rubber and the other synthetics. It is not necessary to conclude from this that the reinforcing properties of a filler should, at a given particle size, be independent of its chemical nature, for the interaction between rubber and filler will play a two fold part. Firstly, by analogy with the wetting of solids by liquids, a high filler-rubber interaction will increase the dispersion and reduce the tendency to flocculation, and secondly it implies that more work must be done to separate the rubber from the filler. This is supported by the
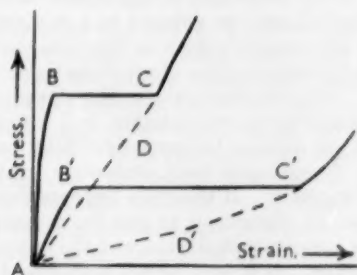

Fig. 14.

recently published data on the effect of heat treatment of carbon blacks without altering their size, where a modification of the surface alters the physical properties.

The results observed in the present work can be interpreted in terms of the work required for dewetting the filler particles.

Consider Figure 13 in which are shown two stress-strain curves for vulcanizates differing only in the particle size of the filler. It is assumed that complete dewetting has taken place at the end of the plateau, and that, to a first approximation, the completely dewetted material has the same curve in each case.

The dotted line represents the curve which would be obtained on allowing the specimens to retract from C or E.   Then the energy required for dewetting is given by the areas ADEFA and ABCFA.

If the energy required to dewet unit area of the filler is roughly constant and independent of particle size then more energy is required for the small particle specimen and so area ADEFA is greater than ABCFA, as observed.

Similarly, at a given elongation, it is seen that a larger fraction of the energy required for complete dewetting will have been expended with the large particles. This is confirmed by the observation of Jones and Yiengst that at a given elongation a larger percentage of large particles have visible vacuoles than with small particles.

The effect of modulus is shown in Figure 14, which shows the same mix with different degrees of cure.

The energy required for complete dewetting is seen to be represented by the areas ABCDA and AB'C'D'A.   Provided that the energy of dewetting is independent of the degree of cure these areas should be equal, and hence the higher the modulus the higher the plateau, as observed.

EXPERIMENTAL VERIFICATION OF MODULUS EQUATIONS

Previous work on filler reinforcement has fallen into two many categories, namely the derivation and testing of equations relating the modulus of a filled rubber to its filler content (e.g., ref. 4) and technological work relating the usual criteria of reinforcement to specific properties of fillers, e.g., particle size[5].   In the light of the data presented here is it possible to lay down some conditions with which the experimental data to test the modulus equation should comply.

It is clearly important that the filler should be well dispersed in the rubber since inadequate dispersion leads to a lowering of modulus, either by a specific effect of particle size, or by dewetting of aggregates acting as large particles. Secondly, dewetting itself should be reduced to a minimum since when it has occurred the effective filler concentration is then less than stoichiometric.   It seems common to most fillers that at low elongations the slope of the stress-strain curve is initially high, and then decreases as the elongation increases, in contrast to the behavior of pale crepe vulcanizates, or if dewetting is not occurring, at a given elongation, the rubber between rigid filler particles must be at a higher elongation than the specimen itself, and hence crystallization will appear at a lower apparent elongation.   It therefore appears that the modulus should be measured at as low an elongation as can be accurately measured.   The practice of prestressing appears undesirable, and the criterion for lack of dewetting would be reversibility.   It is well known that repeated stretching to high elongations has a very marked effect on modulus (e.g., ref. 6) and while primary and secondary filler-rubber bonds have been postulated it appears equally probable that, with very fine carbon blacks, the effects are due to the progressive dewetting of small aggregates, the dispersed individual particles remaining stuck to the rubber.

Volume change and stress-strain measurements have indicated that with large particles more dewetting takes place than with small ones, and hence to test the various equations a very fine particle filler should be used.   Also, the stress decays with time in a filled specimen maintained under tension, the greatest rate of decay occurring in the first few seconds, the apparatus used by Guth[7] overcoming this objection.

It therefore appears that any experiments to test the theories should:

(a) Use small particles well dispersed.
(b) Measure stresses at very low elongation.
(c) Measure the stress immediately the elongation is reached.

SUMMARY

Examination of the stress-strain curves of vulcanizates containing up to 60 per cent by volume of mineral filler of particle size greater than $1\,\mu$ has led to the discovery of a plateau at which the elongation increases several hundredfold at constant stress.   This has been demonstrated for a number of fillers with several rubbers, natural and synthetic.   The effect of filler content, particle size, and degree of cure on the stress at which the plateau occurs, and its length, have been investigated.   An explanation is suggested and the significance of the observations for the experimental verification of equations relating modulus to filler content is pointed out.

The volume changes accompanying the elongation of these vulcanizates have also been investigated at varying filler contents, particle sizes, and degrees of cure, and shown to correlate with the stress-strain curves.

The possible bearing of these results on the nature of the rubber-filler bonds, and hence on the reinforcing action of fillers, is briefly discussed.

ACKNOWLEDGMENTS

CONFERENCE DISCUSSION

Dr. NAUNTON recalled that in 1951 he and others read a paper at Cleveland dealing with the determination of bond strength by repeated impacts.   It had been found that when the rubber between the steel faces was a highly filled rubber, it behaved after repeated blows like a gum stock.

Bryant and Bisset were to be congratulated on an extremely interesting and systematic piece of work.   They had explained exactly what happened in their own tensile experiments.   The energy was used to break the bond, and then, having broken the bond, the rubber behaved like a gum stock.

Mr. MULLINS said that the stress-strain behavior of highly filled vulcanizates described by Bryant was of interest, and it would appear that the pronounced plateau which he obtained could be readily interpreted in terms of a progressive breakdown of filler structure resulting from the process breakdown, increase in extension, reduction in area, increase in stress, further breakdown.   In which case it was to be expected that the position and extent of the plateau would depend upon the conditions of test.   Had Mr. Bryant observed any such changes on varying the conditions of test, for example the rate of extension or loading?

Mr. BRYANT, in reply, stated that increasing the rate of elongation to 20 in. per min. (about 640 per cent per min.) raised the plateau slightly without affecting its length, but decreasing the rate to about 10 per cent per minute was without effect.

Mr. BLANCHARD said that Mr. Bryant's paper was a valuable contribution

on the effects of fillers in rubber. The discovery of a stress-plateau, and its explanation by progressive breakage of filler-rubber bonds, could be readily appreciated. It should, he thought, be made clear that this plateau did not measure the resistance to detaching rubber from filler; in fact, the authors stated that it could be raised by increasing the modulus of the rubber matrix. He suggested, therefore, that the higher stress plateau for smaller particles did not show that these were more resistant to separation from the rubber, or that large particles would become detached before small ones. The question then arose as to how far such conclusions could be justified only by the volume changes. Personally, he had doubts on this point.

Caution was necessary in considering the behavior of carbon blacks on the basis of this investigation of other fillers, as Mr. Bryant was most careful to emphasize in presenting his paper. The view that reinforcing action involved an ability of the filler to remain stuck to the rubber could be readily appreciated. Experience with carbon blacks, however, did not show the residual stiffening after high prestresses, or the distribution of linkage strengths, to be related to the mean particle diameter. The greater strength of linkages broken at higher extensions could be related to larger energies dissipated in breaking them.

He did not think that all this could be explained by distributions of particle sizes, or by progressive detachment of small aggregates from the rubber with the dispersed individual particles resisting separation.

Mr. BRYANT, replying, said that dewetting was a complicated process. One of the main planks of his platform was some work done by Jones and Yiengst, who had put filled rubbers under the microscope and painstakingly counted the number of particles of a certain size. They had then counted the number of that size that had vacuoles and were able to show, at a given elongation, that as the particle size fell, so the percentage of particles at that size which had vacuoles decreased. The results in the paper, he thought, confirmed that, although he agreed with Mr. Blanchard that taken by themselves they did not put the matter beyond doubt.

Regarding the plateau effect, there was one point to which he wished to draw attention and on which he would welcome any suggestions. Why did it suddenly show up at about 35 to 40 per cent of filler, and why was the plateau not always obtained? He had a suspicion that it was something to do with the dispersion of the powder, but from the terms of reference of their problem he and his co-author were not able to get powders which they were certain were either completely dispersed or very badly flocculated.

Dr. VAN ROSSEM suggested that the reason for the plateau effect might be quite different from any yet mentioned. He was struck by the similarity of the curves to the tensile curve of gutta-percha, which gave exactly the same plateau; there was no filler in it except for some gutta-percha crystals. During the tensile test, at a certain stage the width of the test basis would suddenly decrease, and this process continued over the whole length. He had not known the English term for this, but during the refreshment interval he had discovered that it was "necking". His own belief was that the plateau effect was caused by the necking of the dumbbell testpieces.

One could go further and ask what was the reason for the necking. It was certainly not that the filler particles were lost from the rubber in what was called dewetting; because it could be seen from Figure 9 that the volume increase was already starting at very small elongations. This meant that small particles had always been lost from the rubber and had never been wetted by the rubber.

Mr. BRYANT, in reply, wished to make it clear that any necking during the work was entirely confined to the rubber mixes. He agreed with Dr. van Rossem's remarks about the experimental curves. The paper suggested that the GR-S was a stiffer gum stock than natural rubber, that the dewetting began at a smaller elongation, and it did not show up in the curves in the paper. With a very coarse particle, however, one could actually rub the particles off the surface, but he agreed that the degree of adhesion to materials like GR-S was very low, because the plateau was low.

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RUBBER REINFORCEMENT BY RESINS FORMED IN LATEX *

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INTRODUCTION

Many attempts have been made to combine synthetic resins with rubber. In most cases the resins were incorporated in the dry rubber on the mill[1] and some success has been obtained with thermoplastics, such as high-styrene resins[2]. Phenolic resins are compatible with nitrile rubbers, but not with GR-S or natural rubber[3]. Therefore, attempts have been made to incorporate the resin in an unhardened state and to harden it afterwards in the rubber[4]. In this way rubber can be vulcanized[5]. Such incorporation causes difficulties; an alternative is to mix emulsions of resins with latex and to coprecipitate the resin and the rubber[6], or to dissolve the partly condensed and still soluble phenolic resin in a caustic soda solution and to mix this solution with latex so as to precipitate the resin and rubber at the same time by the addition of acid. The products obtained after vulcanization were, however, far from satisfactory[7]. Somewhat better results were obtained when the latex was not coagulated but evaporated[8], and thus the resin partly formed in situ. This method, the formation of the resin in situ, has been followed by some investigators[9] and most success has been obtained by Le Bras and Piccini[10], using an alkaline solution of a partially condensed resorcinol-formaldehyde resin, which is mixed with trypsinated, heat-sensitized latex and vulcanizing ingredients. Products with remarkable properties, especially with a high tensile strength and a very high tear resistance were obtained, when the latex was gelatinized, dried, and vulcanized. Their method is a method of latex-reinforcement and the reinforcement disappears completely when the dried but not yet vulcanized product is brought on the mill. For the sake of completeness it may be mentioned that trials have also been made to introduce resins into rubber by polymerizing suitable vinyl derivatives in latex[11].

PREPARATION OF RESIN-REINFORCED RUBBERS

Until recently the only resins that could be prepared in latex were those that could be prepared in alkaline solution and even then the ingredients required for the formation of the resin often coagulated the latex.

It is therefore of interest to find that many resins can be formed in latex which has been stabilized against acid by means of cationic or nonionic stabilizers.

Thus materials can be prepared without difficulty containing different percentages of condensation resins with formaldehyde, formed in aqueous acid solution, e.g., with aniline, substituted anilines, urea, thiourea, dicyandiamide,

TABLE I

RESIN-RUBBER PRODUCTS CONTAINING ANILINE-FORMALDEHYDE RESIN PREPARED FROM 1 MOL. ANILINE; 1½ MOL. FORMALDEHYDE

On 100 rubber, 5 ZnO, 1 Nonox, 0.25 di-n-butylamine, 1 zinc dibutyl dithiocarbamate, 1 Zn stearate, 2 S

% Resin	10	15	20	25	30	40	50	60	For comparison 33% of furnace black (EPC)*
Optimum time of vulcanization at 100°C	30'	45'	45'	45'	30'	45'	45'	45'	
Tensile strength, kg./cm.²	392	348	370	375	346	178	139	134	325
Elongation at break, %	634	545	520	525	500	188	156	50	548
Modulus 300%, kg./cm.²	73	108	150	175	186	—	—	—	118
Modulus 500%, kg./cm.²	168	311	355	370	—	—	—	—	283
Hardness Shore A	45	53	63	63	70	87	88	97	64
Elasticity Shore	75	85	70	57	48	42	30	25	63
Heat build-up at 20°C after 30'	26	10	20	43	76				45
Lüpke resilience, %	83	83	74	65	57				52
Flex cracking cycles × 10³	40	108	88	46	18				61
Tear strength, Delft method, kg./cm.²	82	92	108	160	159	40	39	Not measurable	188
Tensile strength at 100°C kg./cm.²	124	127	121	202	116				190
Elongation at break at 100°, %	587	365	350	540	512				866
Tear strength at 100°C	29	31	31	60	59				100
Abrasion loss Grasselli, mm.³/kg.	0.44	0.65	0.59	0.62	0.39				0.73
Bierer Davis, 7 days: Tensile strength, % decrease	48	33	38	51	68				62
Elongation at break, % decrease	19	19	32	49	68				
Swelling benzene vol., %	267		253		127	146	163	125	30
Swelling petrol vol., %	187		152		139	88	94	53	200
Brittle point, °C	-62		-60		-58	-45	-38	>+20	103
Specific gravity	1.00	1.03	1.03		1.04	1.08	1.10	1.13	-60

* On 100 rubber, 5 ZnO, 2.5 S, 2 stearic acid, 3 pinetar, 1 phenyl-2-naphthylamine, 0.9 N-cyclohexylbenzothiazole-2-sulfenamide, 50 carbon black EPC. Vulcanization 45' at 127°C.

guanidine, melamine, resorcinol, phloroglucinol, *m*-aminophenol, and also with mixtures of these.

Although the latex is stabilized the rubber coagulates along with the resin as soon as the latter is fully condensed.   Thus, after the formation of the resin the whole mass can be crumbled, leached with ammonia, washed, and dried.   The product can be mixed on the mill with vulcanizing ingredients, and fillers, and vulcanized by means of ordinary methods.   In this way products with remarkable properties can be obtained.

It may be stressed that although the compound is prepared in latex, this method results in reinforcing dry rubber products as distinct from the method of Le Bras-Piccini, mentioned above, which is a method for the reinforcement of

FIG.1   STRESS—STRAIN DIAGRAM OF RUBBERS CONTAINING ANILINE RESIN
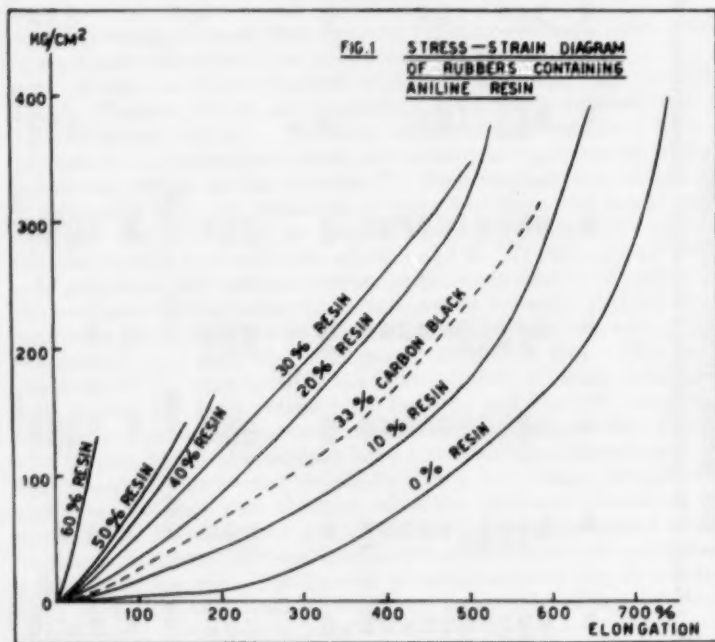
latex products.   Now some examples may be given in somewhat more detail. It may be stated beforehand that in these examples the Hevea latex may be replaced by GR-S latexes.

Compound containing 30 per cent aniline-formaldehyde resin and 70 per cent rubber.—11.66 kg. of 60 per cent latex is mixed with 1 liter of 20 per cent aqueous Emulphor-O and neutralized with about 1.2 l. of 4 N hydrochloric acid. To this, 2.46 kg. of aniline in 10 l. of water and 2.65 l. of concentrated hydrochloric acid is added.   Then 4.8 liters of 33% formaldehyde solution diluted with 10 liters of water is quickly added while stirring vigorously.   As soon as the color of the reaction mixture begins to turn yellow the stirring is stopped. The temperature rises to about 40° C, the mass turns reddish-brown and gelatinizes.   The product is kept for about an hour, then divided into small pieces and leached for about 16 hours in 40 l. of 4 N ammonia, during which the
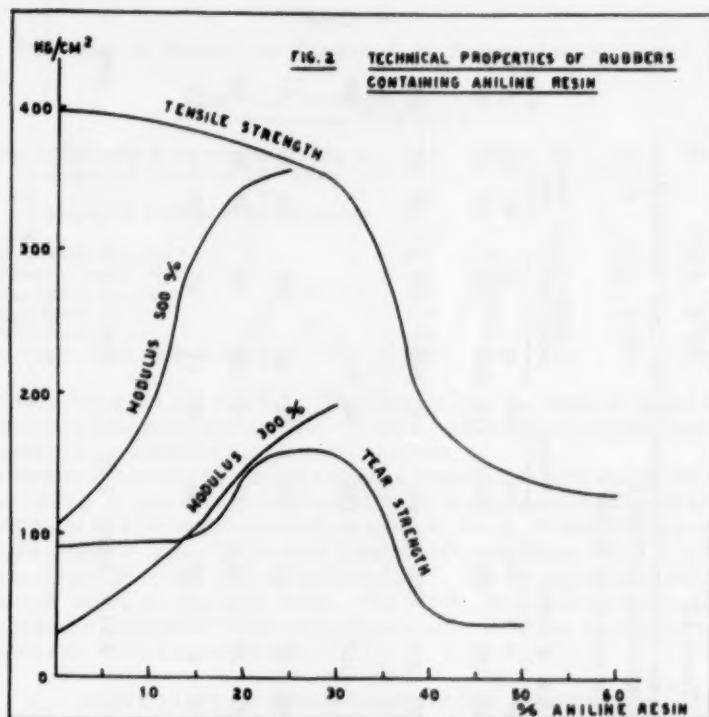
color becomes yellowish-white. It is filtered, washed, and dried at 40° to 100° C. Then the necessary vulcanizing ingredients are incorporated on the mill and finally the product is press-cured.

Compound containing 30 per cent urea-formaldehyde resin and 70 per cent rubber.—83 g. of urea is dissolved in 210 cc. of 33 per cent formaldehyde solution; 390 g. of latex (60 per cent) is stabilized with 40 cc. of 20 per cent aqueous Emulphor-O solution, neutralized with 4 N hydrochloric acid and enough acid

TABLE II

RESIN-RUBBER PRODUCTS CONTAINING 20 PER CENT ANILINE-FORMALDEHYDE RESIN VULCANIZED AT DIFFERENT TEMPERATURES

On 100 rubber, 5 ZnO, 1 N-cyclohexylbenzothiazole-2-sulfenamide, 1 stearic acid, 1 phenyl-2-naphthylamine, 2 S, 2 Dutrex 3

	127°	142°	157°
Vulcanization temperature, ° C	127°	142°	157°
Vulcanization time (optimum)	60′	20′	10′
Tensile strength, kg./cm.^{2}	380	376	344
Elongation at break, %	600	625	600
Modulus 300%, kg./cm.^{2}	118	107	97
Modulus 500%, kg./cm.^{2}	279	258	253
Hardness Shore A	68	66	66
Elasticity Shore	63	66	65
Tear strength, Delft method:			
// Direction of calendering, kg./cm.^{2}	157	171	129
⊥ Direction of calendering, kg./cm.^{2}	154	151	157

TABLE III

INFLUENCE OF VARIOUS FILLERS ON RESIN-RUBBER PRODUCTS CONTAINING 30 PER CENT ANILINE RESIN

Vulcanizing ingredients, see Table I

Optimum time of cure 30–45' at 100° C

Parts (by weight) on 100 rubber resin (70 rubber-30 resin)	Frantex		Franclay		Hi-Sil		Silene		Whiting		EPC, carbon black		Wood flour		Without filler
	30	60	30	60	30	60	30	60	62	122	45	90	66	132	
Tensile strength, kg./cm².	244	139	234	159	101	68	167	108	184	111	248	193	86	80	346
Elongation at break, %	375	290	400	300	300	233	300	229	440	330	340	250	125	50	500
Modulus, 300% kg./cm².	204		170	159	101		167		106	90	222				186
Hardness, Shore A	85	93	85	88	90	98	87	92	77	81	85	93	95	99	70
Elasticity Shore	30	27	35	30	25	27	28	32	45	38	34	30	38	52	48
Tear strength. Delft method, kg./cm².	117	50	86	53	41	52	51	55	84	30	61	47	59	—	159
Abrasion loss* Grasselli mm.³/kgm.	1.72	2.92	3.38	3.89			3.39	3.32	5.43		2.26	2.20			0.89

* Another machine was used as in Table I.

TABLE IV

INFLUENCE OF AEROSIL AND VULCSAIL C ON RUBBER–ANILINE RESIN
PRODUCTS

Vulcanizing ingredients, see Table II
Vulcanization 30′ at 142° C

Per cent aniline resin in resin-rubber products	10	20	20	30	30
Parts (by weight) of Aerosil on 100 rubber + resin	44	44	—	44	—
Parts (by weight) of Vulcasil C on 100 rubber + resin	—	—	39	—	39
Tensile strength, kg./cm.^{2}	233	186	227	168	127
Elongation at break, %	435	283	360	250	150
Modulus 300%, kg./cm.^{2}	154	—	190	—	—
Hardness Shore A	79	90	87	88	94
Elasticity Shore	58	43	47	35	32
Tear strength, Delft method, kg./cm.^{2}	129	132	112	78	59

is added to bring the pH below 1. The solution and the latex are mixed and the mixture is left standing overnight. A white resin forms which is neutralized with ammonia and worked up as described above.

Compound containing 30 per cent melamine-formaldehyde resin and 70 per cent rubber.—125 g. of melamine is dissolved at 90° C in a mixture of 240 g. of water and 240 cc. of 36.5 per cent formaldehyde; 584 g. of latex (60 per cent) is stabilized with 37.5 cc. of 20 per cent Emulphor-O, neutralized with 4 N hydrochloric acid and 30 cc. of 5 per cent acid is added. The melamine-formaldehyde solution is added to the acid latex. The whole mass gelatinizes in some minutes and is kept at 80° C for about 30 minutes. It is then neutralized with ammonia and worked up as stated.

PROPERTIES OF RESIN–REINFORCED RUBBERS

In general, it can be said that when the resin content of the products is about 60 per cent or less, they can be worked on the mill. Above 60 per cent resin powders are obtained, and in some cases it was found that they could be used as molding powders.

When vulcanized, the products containing up to 30 per cent resin are rubberlike materials; with 30 to 50 per cent resin they become increasingly tough and leatherlike, and with higher resin content they resemble plastics and break on bending.

The aniline resin-rubber mixtures have been studied extensively, and their technological properties can be seen from Table I and from Figures 1 and 2.

TABLE V

RESIN–RUBBER PRODUCT CONTAINING 30 PER CENT
UREA–FORMALDEHYDE RESIN

On 100 rubber, 5 ZnO, 1 stearic acid, 0.5 Styphen I (a non-discoloring
antioxidant), 2 sulfur, and 1 N-cycloheyxlbenzothiazole-2-sulfenamide
Vulcanization 20′ at 142° C

Tensile strength, kg./cm.^{2}	274
Elongation at break, %	650
Modulus 300%, kg./cm.^{2}	59
Modulus 500%, kg./cm.^{2}	169
Hardness Shore A	53
Elasticity Shore	59
Tear strength, Delft method, kg./cm.^{2}	112

FIG. 3   STRESS—STRAIN DIAGRAM
OF RUBBERS CONTAINING
VARIOUS RESINS
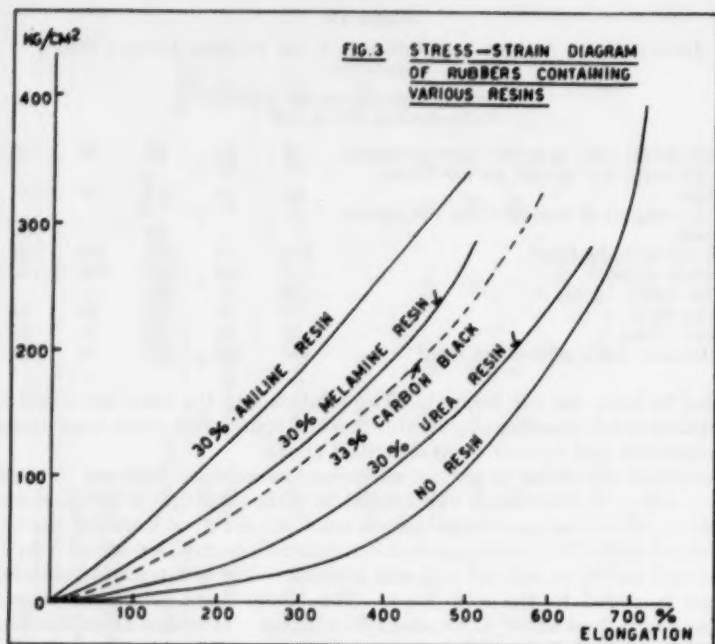
Products with analogous properties were obtained by using other accelerators, such as benzothiazolyl disulfide + A-32, diphenyl guanidine with benzothiazolyl disulfide or N-cyclohexyl-benzothiazole-2-sulfenamide. For example, see Table II.

From these tables it appears that products with a high modulus and a high hardness can be obtained. In comparison with a carbon black mixture of about the same hardness, a product with 20 per cent aniline resin has lower heat buildup and far better Lüpke resilience.

Harder, and somewhat more "dead" or cheaper material, can be obtained by incorporating different fillers on the mill and the Tables III and IV give some examples of such products.

All these products, both the filled and the unfilled, are yellow and can be

TABLE VI

RESIN–RUBBER PRODUCT CONTAINING 30 PER CENT MELAMINE
RESIN PREPARED IN LATEX

On 100 rubber, 5 ZnO, 1 stearic acid, 1 N-cyclohexylbenzothiazole-2-
sulfenamide, 1-phenyl-2-naphthylamine, 2 sulfur.
Vulcanization 60' at 127° C

Tensile strength, kg./cm.²	292
Elongation at break, %	500
Modulus 300%, kg./cm.²	137
Modulus 500%, kg./cm.²	292
Hardness Shore A	70
Elasticity Shore	58
Tear strength	125

TABLE VII

GR–S ANILINE RESIN PRODUCTS, TYPE LATEX II, TOTAL SOLIDS 26.8%, STYRENE CONTENT OF THE RUBBER 23.5%

On 100 rubber, 5 ZnO, 2 stearic acid, 1.5 phenyl-2-naphthylamine, 4 Dutrex 3,
0.8 benzothiazolyl disulfide, 0.2 A32, 2 sulfur
Vulcanization 30′ at 142° C

Aniline resin, %	0	10	20	30	40	50	60
Tensile strength, kg./cm.²	19	72	133	187	127	79	85
Elongation at break, %	331	556	471	558	390	96	50
Modulus 300%, kg./cm.²	15	27	66	93	104	—	—
Modulus 500%, kg./cm.²	—	65	—	161	—	—	—
Hardness Shore A	45	50	68	82	85	93	100
Elasticity Shore	88	70	50	35	35	30	<20
Tear resistance, kg./cm.², Delft method	8	18	39	57	58	50	—

made in different colors, but have the drawback that in light they turn brownish yellow to brown even when containing a nondiscoloring antioxidant.

The products with urea-formaldehyde resin are white and color-stable in sunlight (if containing a nondiscoloring antioxidant), but have the disadvantage of a rather low modulus (Table V).

Far better products, which are also white and nondiscoloring, can be obtained with melamine-formaldehyde resin (Table VI and Figure 3).

The properties of the many other resin-rubber combinations prepared according to the method described were mostly inferior to those of the examples given. It was especially detrimental to the technical properties of the aniline resin-rubber compounds to replace a part or the whole of the aniline by *ortho-*, *para-* or *N*-substituted anilines. However, the properties remained about the same when part of the aniline was replaced by *meta*-substituted anilines as *meta*-toluidine.

Further, it should be mentioned that it is not necessary to use 60 per cent latex. With fresh diluted field latex (DRC 14.41 per cent) and even with skim latex (DRC 7.39 per cent) products with 20 and 30 per cent aniline resin were made which showed the same properties as those prepared from 60 per cent latex.[12]

Synthetic rubbers also can be reinforced by these resins. As an example, Tables VII and VIII and Figures 4 and 5 show the results of the incorporation of resins (prepared in the latex) into GR-S type II.

TECHNICAL USES

Experiments on the technical use of these resin rubbers were first made with aniline resin-rubber mixtures.

TABLE VIII

GR–S RESIN PRODUCTS. TYPE LATEX II, TOTAL SOLIDS 26.8, STYRENE CONTENT OF THE RUBBER 23.5%

Vulcanizing ingredients, see Table I
Vulcanization 30′ at 100° C

Type of resin	30% Urea-formaldehyde	30% Melamine-formaldehyde
Tensile strength, kg./cm.²	26	118
Elongation at break, %	46	300
Hardness Shore A	93	68
Elasticity Shore	24	63
Tear resistance, kg./cm.², Delft method	28	38

FIG. 4   TECHNICAL PROPERTIES OF GR-S TYPE II CONTAINING ANILINE RESIN
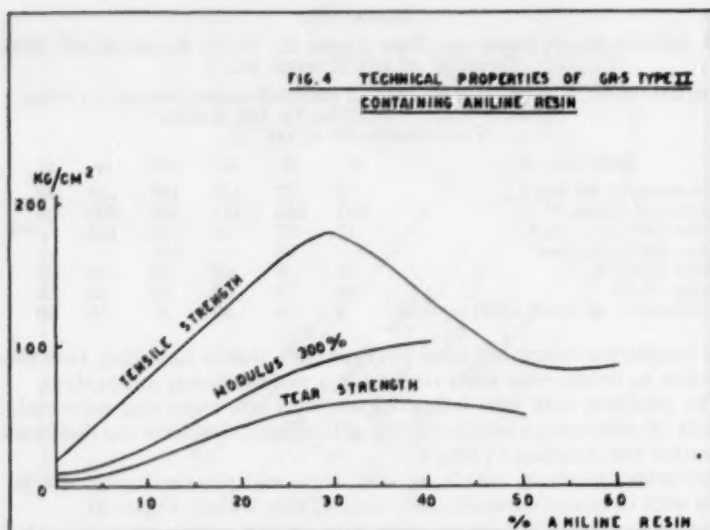
The products containing higher percentages of resin are rather tough and require more power on the mill, but this can be diminished substantially when the latex is mixed with an emulsion of 3 per cent Dutrex-3 (a hydrocarbon oil) and/or 0.5 per cent Pepton 22 (a peptiser), all percentages being calculated on the rubber.

FIG. 5   STRESS—STRAIN DIAGRAM OF GR-S TYPE II CONTAINING VARIOUS RESINS
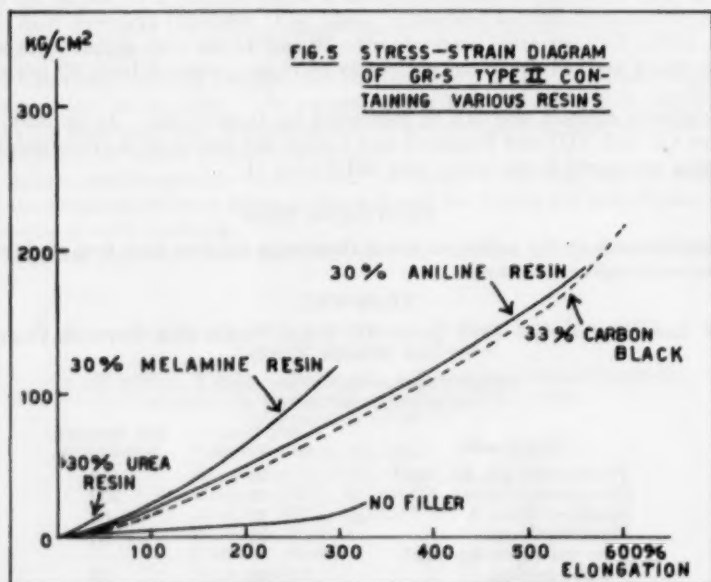
The mixtures can be vulcanized in the ordinary way.

Application in soles.—Experiments on soling were made for the most part with aniline-resin rubber products.

The selling points of these materials would be:

(1) The materials are light colored and can, if desired, be given a leatherlike appearance.

(2) The soles do not stain carpets or wooden parquet floors.

(3) Hard products can be obtained giving the same "foot comfort" as leather.

(4) The soles do not spread (as polyvinylchloride soles may).

(5) The abrasion resistance is high and in actual wearing tests it was comparable with that of a good carbon black compound (tire treadstock).

(6) The soles can be stuck and stitched.

(7) If desired, these soles can have a certain deadness or can be made more elastic.

(8) The tear resistance is much better than that of the styrene resin—or cyclized rubber compounds—and is comparable with that of a carbon black compound.

(9) The products are likely to be cheaper than leather.

The products can be used not only as soling but also in the form of a relatively thin upper sole (dump sole) covering and protecting a leather sole.

Actual wear trials showed that the wear resistance of the mixtures of 100 parts of rubber product (containing 30 per cent of aniline or melamine resin) and 30 parts of Frantex was very good.

Cellular soles could be made by the addition of a blowing agent to the 15/85 aniline resin rubber.

Application in tires.—Much work has been done at the Rubber-Stichting and the Institut Français du Caoutchouc on the use of the new resin-rubber compounds for tires.

The mixture can easily be extruded, the mixtures with 20 to 30 per cent resin giving a remarkably smooth surface.

Without any difficulty a tire was recapped with a 20/80 aniline resin-rubber compound. The adhesion to the carcass was excellent. The tire ran about 1200 km. without visible faults and the conclusion was that this aniline resin recapped tire abraded about 33 per cent quicker than a carbon black (50 Vulcan 3/100 r.) tire. At the Institute Français du Caoutchouc, twenty tires were built using a 25/75 aniline resin-rubber composition containing 2 per cent of Dutrex V4 and 2 per cent carbon black as a tread material.

Twelve of these tires are running on ordinary passenger cars and up till now it seems that their life expectation is about 20,000 to 30,000 km. in normal circumstances.

THEORETICAL PART

Different views can be held concerning the question as to which property of rubber must be improved by the filler before one may speak of a reinforcing filler. Resins prepared in latex (e.g., aniline-formaldehyde resin and melamine-formaldehyde resin) are indisputably reinforcing fillers in that they enhance the same properties as does carbon black in both natural rubber and GR-S. The particles of a reinforcing carbon black are, however, so small that they can be seen only by means of an electron microscope. The resin in the resin-filled rubbers is much coarser and a regular structure in resin rubber can easily be observed by means of an ordinary microscope (cf. Figures 6, 7, and 8).
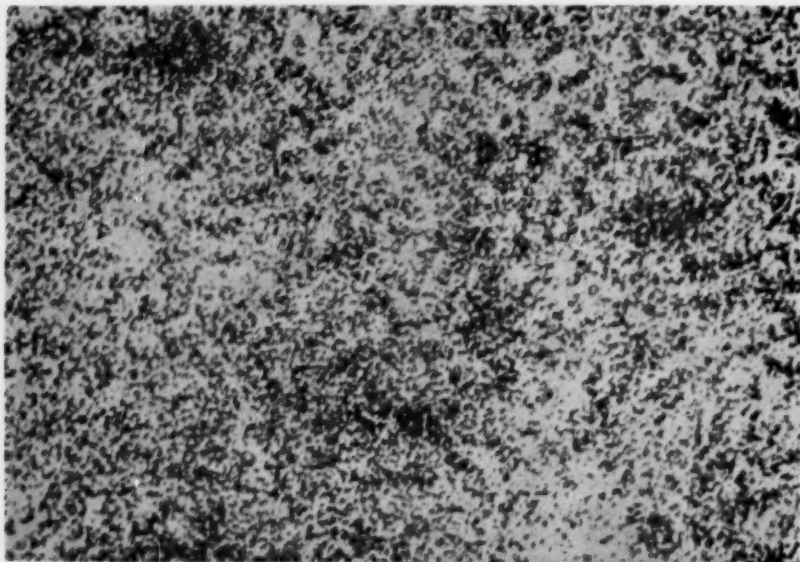
FIG. 6.—(Magn. 1000 ×.) Rubber containing 30 per cent aniline resin prepared in latex. Plasticized but not vulcanized. Swollen in benzene. Dyed with iodine in benzene.
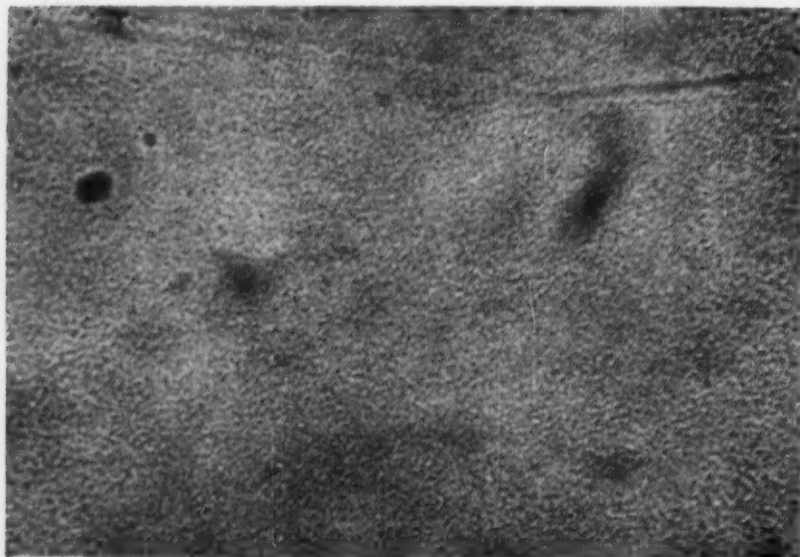
FIG. 7.—(Magn. 1000 ×.) Rubber containg 30 per cent aniline resin prepared in latex. Vulcanized. Slightly swollen in benzene. Dyed with iodine in benzene.

Now the question can be posed: Why are these resins reinforcing fillers? In order to answer this question tests were carried out with the aniline resin products, and according to the author the results show that there must be chemical bonds between the resin particles and the rubber molecules. The evidence is in four classifications: First, it is well known that rubber in latex can react with formaldehyde under the influence of acid[12] and therefore it is reasonable to assume that during resin formation the formaldehyde binds resin molecules to rubber molecules. Second, in order to obtain the full reinforcing effect of the resins it is necessary to prepare them in latex. If the resins are mixed in on the mill, or when an aqueous dispersion of the fully formed resin is mixed with latex, the modulus, tensile strength, hardness, and especially the tear resistance of the vulcanizates are much lower in value (cf. Figures 7 and 8).
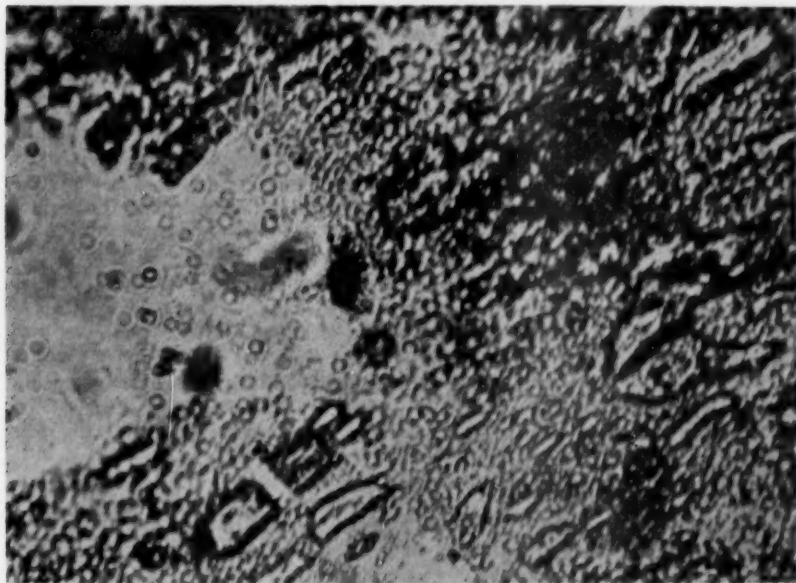
FIG. 8.—(Magn. 1000 ✕.)   Rubber containing 30 per cent aniline resin, mixed in as a powder in the dry rubber on the mill.   Vulcanized.   Slightly swollen in benzene.   Dyed with iodine in benzene.

Third, when the resins are formed in the stabilized latex they precipitate the rubber from the latex and the formation of even as small an amount as 0.5 per cent aniline resin in 60 per cent latex stabilized with Emulphor-O precipitates the rubber completely. Thus, if in acidified latex a resin soluble in hydrochloric acid is prepared from 1 mole aniline and somewhat less than 1 mole formaldehyde, there is no precipitate, but resin and rubber will precipitate when ammonia is added. If, however, this resin solution is prepared separately and mixed with stabilized latex (in the same amount) and ammonia is then added, no rubber, and even no resin, precipitates. This proves that chemical bonds are formed between the resin and the rubber only when the resin is formed in the latex. The fact that the rubber is precipitated with resorcinol resin in an acid as well as in an alkaline medium seems to exclude the supposition that this precipitation is an electrocolloidal phenomenon. Aniline resin is not formed

in an alkaline medium so resorcinol is cited as an example. On the other hand, precipitation of silicic acid in stabilized latex does not precipitate the rubber. Ordinary and protein-free latexes require just the same amount of aniline resin for precipitation, eliminating the possibility that the protein layer on the latex globules is responsible for the phenomenon. Finally, from the dried gel obtained by the formation of aniline resin in latex only a small fraction of the rubber can be extracted by benzene, and even if the product is plasticized, less than 45 per cent of the rubber can be extracted from a material containing 30 per cent resin. On the other hand, many experiments prove that the chemical composition of the resin also has a very great influence. With aniline resin the technological properties deteriorate when the relative amount of formaldehyde is lowered below 1.5 mole on 1 mole of aniline or when part or the whole of the aniline is replaced by substituted anilines as p-toluidine, or m-aminophenol. In this connection attention is drawn to urea-formaldehyde resin. This is prepared in latex in just the same way as aniline resin, but its reinforcing properties are certainly less.

SYNOPSIS

Polycondensation resins can be formed in acidified latex stabilized with non-ionic or cationic stabilizers by adding the necessary ingredients to the latex.

The rubber is coagulated at the same time, and the product is neutralized, dried, and worked up like dry rubber. There are indications that the resin is chemically bound to the rubber.

Rubbers prepared in this way, containing up to 30 per cent aniline-formaldehyde resin or melamine-formaldehyde resin, have properties comparable with those of carbon black compounds, except for their light color. With 40 to 50 per cent resin the products are tough and leatherlike and with 50 to 60 per cent resin they somewhat resemble flexible plastics.

The products with 20 to 30 per cent resin have already been tested as sole and tire materials.

Not only natural, but also synthetic rubbers, are reinforced by resins prepared in this way.

ACKNOWLEDGMENT

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13 Dutch 45,722. Unpublished work by S. von der Meer at the Rubber-Stichting has shown that at ordinary temperatures rubber reacts with aqueous formaldehyde and hydrochloric acid.

LIGNIN AS A COMPOUNDING INGREDIENT FOR NATURAL RUBBER *

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INTRODUCTION

Important claims have been made in recent years regarding the capacity of lignin to reinforce natural and synthetic rubber. In 1949 Dawson[1] reviewed the literature on the use of lignin in rubber and drew particular attention to the work of Keilen and Pollak[2] who had shown that in certain circumstances lignin could be considered to rival EPC black in its ability to yield strong GR-S vulcanizates with high resistance to tear.

Raff and his coworkers[3] subsequently showed that the reinforcement of GR-S by lignin is enhanced if the lignin, before coprecipitation with the latex, is subjected to oxidation; other workers studied the application of lignin to the reinforcement of different elastomers[4], the influence of coprecipitation conditions on the properties of the product[5], and the problem of overcoming the delaying effect of lignin on vulcanization of lignin-natural rubber coprecipitates[6].

Keilen and Pollak in their experiments incorporated lignin into rubber by coprecipitation at the latex stage, but they indicated that similar results could be obtained if lignin "in the gelled state" was added to rubber by milling. No reinforcement was observed however when lignin was added to rubber as a dry powder.

Lignin is potentially an abundant and cheap material which according to the above claims should extend the range of useful compounds available to rubber manufacturers. The present paper describes work undertaken to gain first-hand knowledge of the technique of coprecipitating lignin with natural rubber from preserved latex, to learn something about the properties of natural rubber compounds prepared from lignin coprecipitates, and to study possible ways of incorporating lignin into rubber by means other than coprecipitation. It also records test results for masterbatches prepared by the Rubber Research Institute of Malaya from fresh latex on a pilot plant scale.

TYPES OF LIGNIN

Lignin, the constituent of wood in which cellulose fibers are embedded, occurs industrially in the waste liquors of the chemical woodpulp industry from which it is rarely recovered. Three main processes are in large scale use for separating lignin from wood cellulose: the acid sulfite process, in which lignin is converted into soluble lignin sulfonates by digestion with bisulfite lye under pressure, and the two alkali processes in which lignin is made soluble by treating wood with caustic soda or with a mixture of caustic soda and sodium sulfide (sulfate process).

On the nature of the structural units present in lignin conflicting views are held. The lignins isolated from wood by chemical treatment differ from one another according to the method of isolation and the botanical source of the ligneous material, and are believed to differ profoundly from undegraded native lignin. It is known, however, that all types of lignin contain hydroxyl groups, both phenolic and alcoholic, some of which are methylated. Sulfate process lignin, by virtue of its treatment with sodium sulfide, is believed also to contain thiol groups.

In the present work alkali-process lignins have been used exclusively because of the ease with which they can be coprecipitated with latex by simple acidification. In what follows, the term lignin without qualification means Indulin A, a pinewood lignin marketed by the West Virginia Pulp and Paper Company, U.S.A. This material is recovered from the waste liquors of the "sulfate" or kraft pulping process by precipitation with carbon dioxide and is stated to be a mixture of thiolignin and alkali lignin relatively free from hemicellulose. It contains 1.4 per cent of sulfur combined as —SH groups.

Another type of lignin used in some of the trials is an experimental straw lignin supplied by Bowaters Development and Research, Ltd. This material (designated "BDR lignin") is prepared from alkaline pulp liquor by precipitation with sulfuric acid at pH 2.5. It contains up to 25 per cent of nonlignin constituents, mainly hemicelluloses, and differs from Indulin A in the degree of substitution of the nucleus and, probably, in having a higher molecular weight (ca. 2×10^4)[7]. As the hemicellulose impurity was found to have little effect on reinforcement, the crude straw lignin was used in the present investigation without purification.

Trials were also made with an oxidized lignin supplied by Howard Smith Paper Mills, Ltd. ("HS oxidized lignin"). According to Raff and Tomlinson[8] mild oxidation causes primarily the formation of carboxyl groupings without serious alteration in the molecular structure of the lignin. The treatment increases the lyophilic properties of the lignin which seemed to be connected with its reinforcing properties in rubber.

PREPARATION OF RUBBER–LIGNIN COPRECIPITATES

Masterbatches of rubber and lignin are usually prepared from a mixture of latex and lignin solution by coprecipitation. Lignin, dissolved in caustic alkali solution, is mixed with latex and the mixture is coagulated with acid. The coagulum is washed in crumb form, or as a coherent sheet (depending on the ratio of rubber to lignin), and is then dried in air. In this way intimate mixtures of rubber and lignin in a wide range of proportions are obtainable, but practical considerations tend to limit the proportions which are normally convenient and useful. When the ratio of lignin to rubber is very high, the coagulated flocs are difficult to filter and wash, and the dry coagulum may be inconveniently hard for subsequent processing.

The first important step in the preparation of rubber-lignin masterbatches is to ensure complete solution of the lignin powder. In the present investigations the lignin was generally ball milled for two hours in caustic soda solution (lignin 20, sodium hydroxide 2, water 78 parts by weight). Optically clear solutions were thus obtained which tended to thicken and gel on standing for long periods. Latex was mixed with lignin solution by vigorous mechanical stirring, usually for about five minutes for batches weighing 1 lb. or more.

Experience showed that coagulating conditions must be chosen with care

and strictly controlled in order to produce a fine, filterable crumb which is easy to wash without loss of lignin. In the preparation of masterbatches from preserved latex, formic or sulfuric acid was added slowly with careful control of pH and coagulation was completed at a temperature of 90–95° C. For most preparations the coagulant was 3 per cent formic acid and sufficient was added to bring the pH to 4.0. The wet crumbly coagulum was drained and washed on a coarse sieve until free from acid, air-dried at 40° C for 4 days and consolidated by blending on the mixing mill. In exploratory trials the ratio of rubber to lignin was normally 91 : 36 but masterbatches were also made with rubber-lignin ratios of 100 : 50, 91 : 72 and 100 : 100.

The procedure used by the Rubber Research Institute of Malaya for preparing masterbatches on a pilot plant scale consisted in adding a 10 per cent solution of lignin (Indulin A) to fresh latex (d.r.c. 30 per cent) and coagulating with a solution containing sulfuric acid (5 per cent) and sodium chloride (5 per cent). The latex-lignin mixture and the coagulant, both at 80–90° C, were run simultaneously, with stirring, into the coagulating vessel. The coagulum was then creped and washed.

TABLE I

EFFECT OF VARYING CONDITIONS OF COPRECIPITATION ON PROPERTIES OF RUBBER–LIGNIN (91 : 36)

Type of lignin	Masterbatches										
	Indulin A						BDR Lignin				
Preparation	A/1	A/2	A/3	A/4	A/5	A/6	B/1	B/2	B/3	B/4	B/5
Temperature of vulc., °C	141	141	141	141	141	140	134	141	141	141	134
Optimum vulc., mins.	20	20	30	30	30	40	30	20	30	30	40
Modulus at 300% elongation, kgm/cm²	39	49	49	32	29	42	42	53	41	50	41
Tensile strength, kgm/cm²	215	230	220	177	170	216	215	202	196	203	202
Resilience at 70° C, %	83.8	78.8	82.0	76.9	68.0	81.1	82.9	86.4	84.2	87.2	79.8
Tear strength, kgm./cm²	126	—	121	—	—	124	116	105	—	—	100

With both fresh and preserved latex it was found that variations in coagulating procedure, or differences in the relative proportions of rubber to lignin in the masterbatches, led to differences which were manifested in the properties of the vulcanized compounds (see next section). In general, Indulin A preparations were more sensitive than BDR lignin preparations to coagulating conditions.

VULCANIZATION OF LIGNIN COMPOUNDS

The evaluation of lignin as a compounding ingredient is based mainly on comparisons with carbon black in tread formulations. Most tread compounds contain up to 28 volumes of black per 100 volumes of rubber. Approximately the same volume loading of lignin (s.g. 1.3) is obtained by adding 36 parts by weight of lignin to 100 parts by weight of rubber. Compounds with this loading of lignin and normal proportions of vulcanizing ingredients are somewhat softer than normal tire tread compounds. A systematic study of the effect of vulcanizing agents led eventually to the use throughout these investigations of the following test formula for investigating the reinforcing properties of lignin preparations: rubber 100, lignin 36, zinc oxide 10, stearic acid 4, sulfur 3, mercaptobenzothiazole 1, tetramethylthiuram disulfide 0.1 (compound No. 2 in Table III).

Typical test results using this formulation are shown in Tables I and II. Table I illustrates the effects of varying methods of preparing masterbatches; all the preparations except No. A/6 were from preserved latex, the differences

between them consisting in minor modifications of the conditions of coprecipitation to facilitate filtering.   Preparation No. A/6 was made from fresh latex in Malaya.   The compounds for which test results are given in Table II were prepared from masterbatches containing different proportions of rubber to lignin.

It is noteworthy that the cure inhibiting properties of lignin reported by Griffith and Macgregor[6] were not observed.   When these workers attempted to vulcanize oxidized lignin-natural rubber coprecipitates with conventional vulcanizing systems (e.g., benzothiazolyl disulfide 1 phr, diphenylguanidine 0.4, sulfur 2) their products showed little sign of cure.   When, however, they included in their compounds oxides of metals that form insoluble sulfides (Pb, Cu, Bi) they obtained satisfactory vulcanization.   To explain these observations they assumed that lignin reacts readily with sulfur during vulcanization and builds up a high concentration of hydrogen sulfide which retards vulcanization; the heavy metal oxide acts by absorbing the excess hydrogen sulfide.

In the present experiments no special difficulty was experienced in vulcanizing lignin coprecipitates without the aid of heavy metal oxides.   The simple test formula already given (compound No. 2) yielded vulcanizates with excellent

TABLE II

EFFECT OF VARYING RATIO OF RUBBER TO LIGNIN
ON PROPERTIES OF COPRECIPITATES

	Indulin A			BDR Lignin		
Rubber/lignin	91/36	91/72	100/100	91/36	91/72	100/100
Temperature of vulc., ° C	141	141	141	134	134	134
Optimum vulc., mins.	20	20	20	30	30	30
Modulus at 300%, elong. kgm./cm.³	29	32	31	42	43	41
Tensile strength, kgm./cm.³	215	205	177	215	217	205
Resilience at 70° C, %	83.8	80.4	80.3	82.9	86.5	83.8
Tear strength, kgm./cm.³	126	100	89	116	97	121
Abrasion loss, cc./1000 revs.	0.354	0.486	0.568	—	0.536	—

tensile and tear strengths.   The addition of litharge to this compound certainly accelerated cure and produced an enhancement of physical properties (compound No. 3) but equivalent results were readily obtained with organic accelerators (see Table III).   Since the litharge-activated compounds tended to be scorchy it was concluded that in the formulation of technical lignin compounds the inclusion of litharge is neither necessary nor desirable.

Tibenham and Grace[9] have shown that excellent physical properties can be obtained by compounding lignin coprecipitates with hexamethylenetetramine (10 per cent calculated on the amount of lignin) and milling at a high temperature.   The precise conditions specified could not be obtained with the equipment available in the present investigation and trials with hexamethylenetetramine were therefore limited to using it as an auxiliary vulcanization accelerator (compound No. 5, Table III).

The test data in Table III relate to trial compounds made with coprecipitates prepared in Malaya from Indulin A and fresh latex (rubber/lignin, 2:1).   The selected compounds include (1) a pure gum mix, (2) the standard test formulation with 36 phr of lignin, (3) No. (2) activated with litharge, (4) No. (2) with an additional amount of secondary accelerator (tetramethylthiuram disulfide), (5) No. (2) with the addition of hexamethylenetetramine, (6) a strongly accelerated formulation proposed by the National Research Council of Canada, (7) a formulation with cyclohexylbenzthiazyl sulfenamide/diphenylguanidine, (8) No. (7) with a higher loading of lignin, (9) a formulation with mercaptothiazole/diphenylguanidine, (10) No. (9) with a higher loading of lignin.

TABLE III

TYPICAL COMPOUNDS OF NATURAL RUBBER AND LIGNIN

Compound No.:	1 Base for No. 2	2 Standard test compound	3	4	5	6	7	8	9	10
Natural rubber (smoked sheet)	100									
Natural rubber (from rubber-lignin masterbatch)	—	28	28	28	28	28	28	28	28	28
Lignin (from masterbatch)	—	72	72	72	72	72	72	72	72	72
Zinc oxide	10	36	36	36	36	36	36	50	36	50
Litharge	—	10	10	10	10	7	7	7	7	7
Stearic acid	4	4	4	4	2	2	2	2	2	2
Mercaptobenzothiazole	1	1	1	1	1	2	2	2	2	1.5
Tetramethylthiuram disulfide	—	—	—	—	—	—	—	—	—	—
Zinc diethyldithiocarbamate	0.1	0.1	0.1	0.5	0.1	—	—	—	—	—
N-cyclohexylbenzothiazole-2-sulfenamide	—	—	—	—	—	1	—	—	—	—
Diphenylguanidine	—	—	—	—	1	0.5	1.5	1.5	1.5	1.5
Sulfur	3	3	3	3	3	2	1.5	1.5	3	3
Hexamethylene tetramine	—	—	—	—	—	—	—	—	—	—
Scorch time at 120° C, mins.	21.0	28.5	8.3	34.5	14.9	4.7	46.3	63.0	12.7	8.4
Temperature of vulc., ° C	134	140	134	134	134	134	134	134	134	134
Optimum vulc., mins.	15	50	20	25	25	15	30	30	20	30

Property (Un-aged / Aged*)	1	2	3	4	5	6	7	8	9	10
Modulus at 300% elong., kgm./cm.²	23 / —	38 / 62	55 / 75	45 / —	56 / 101	67 / —	60 / 81	51 / 78	43 / 65	55 / 80
Tensile strength, kgm./cm.²	209 / —	212 / 200	241 / 217	220 / —	242 / 221	237 / —	249 / 233	218 / 216	218 / 223	207 / 210
Elongation at break, %	684 / —	656 / 560	629 / 560	632 / —	623 / 507	566 / —	607 / 555	632 / 513	649 / 577	607 / 552
Resilience at 70° C, %	93.4 / 91.0	81.9 / 82.5	86.1 / 84.2	82.7 / 82.8	82.8 / 89.4	88.1 / 85.6	83.6 / 86.4	70.7 / 77.5	82.7 / 83.2	75.9 / 74.0
Hardness, BS°	47.3 / 53.3	54.4 / 54.6	57.1 / 58.1	54.3 / 55.5	55.5 / 60.1	60.0 / 59.6	59.6 / 61.1	62.4 / 69.7	52.3 / 56	62.0 / 62.0
Tear strength, kgm./cm.³	56 / —	115 / —	150 / —	144 / —	119 / —	140 / —	116 / —	142 / —	122 / —	134 / —

NOTES.—* Samples were oven aged for 7 days at 70° C. Scorch test; ASTM, D.1077-49T. Tensile strength, elongation at break, and modulus; Standard Scopper ring test. Tear strength; B.S. 903, Part 25 (1950). Resilience; B.S. 903, Part 22 (1950), Dunlop tripsometer. Hardness; B.S. 903, Part 19 (1950).
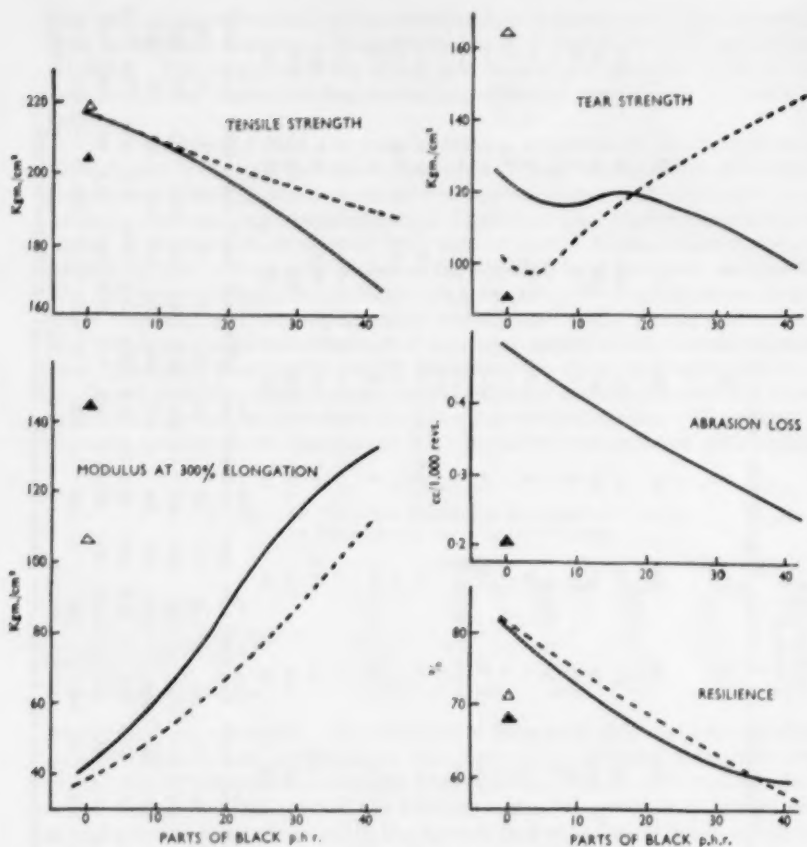
Fig. 1.—Lignin base compound with additions of HAF and MPC blacks. Composition: Rubber, 100; lignin, 36; zinc oxide, 10; stearic acid, 4; M.B.T., 1; T.M.T.D., 0.1; sulfur, 3; black, variable. ——HAF black. - - - - MPC black. ▲, △, denote level of properties given by 50 phr HAF and MPC blacks (respectively), without lignin.

It will be clear from the results that lignin is capable of imparting to rubber high tensile and tear strength and high resilience combined with excellent resistance to aging.

LIGNIN IN CONJUNCTION WITH CARBON BLACK

The precise definition of reinforcement is controversial but undoubtedly involves increased resistance to rupture. In tensile and tear strength the behavior of lignin is similar to that of carbon black but in abrasion resistance it is markedly inferior. The association of high strength with high abrasion resistance which is usually encountered in reinforced rubbers is not found in lignin compounds. The combination of properties obtainable by using lignin and carbon black in conjunction is therefore of special interest. Two series of experiments were made: in the first, rubber with 36 phr of lignin was loaded

with different amounts of two types of black, an MPC black (Micronex) and a HAF black (Philblack O). The rubber-lignin base stock was prepared as a masterbatch from preserved latex and the black was added on the mill. In the second series the total volume of lignin and MPC black was kept constant (28 volumes phr) and the ratio of lignin to black changed over a range of proportions from all lignin to all black. In this case the black as well as the lignin was introduced into the compound in the form of a masterbatch precipitated from latex.

The results of the first series of experiments are shown in Figure 1 and of the second series in Figure 2.

The remarkable feature of the results of the first series (Figure 1) is that rubber already loaded with lignin can be still further loaded with carbon black without serious detriment to tensile and tear strength and with marked improvement in resistance to abrasion. Thus, compounds exhibiting desirable mechanical properties at unusually high volume loadings can be obtained with suitable combinations of lignin and reinforcing blacks. To illustrate this effect Table IV shows some of the physical properties at optimum cure of compounds containing different combinations of lignin and HAF black. At load-

(Lignin decreasing → MPC Black increasing →)
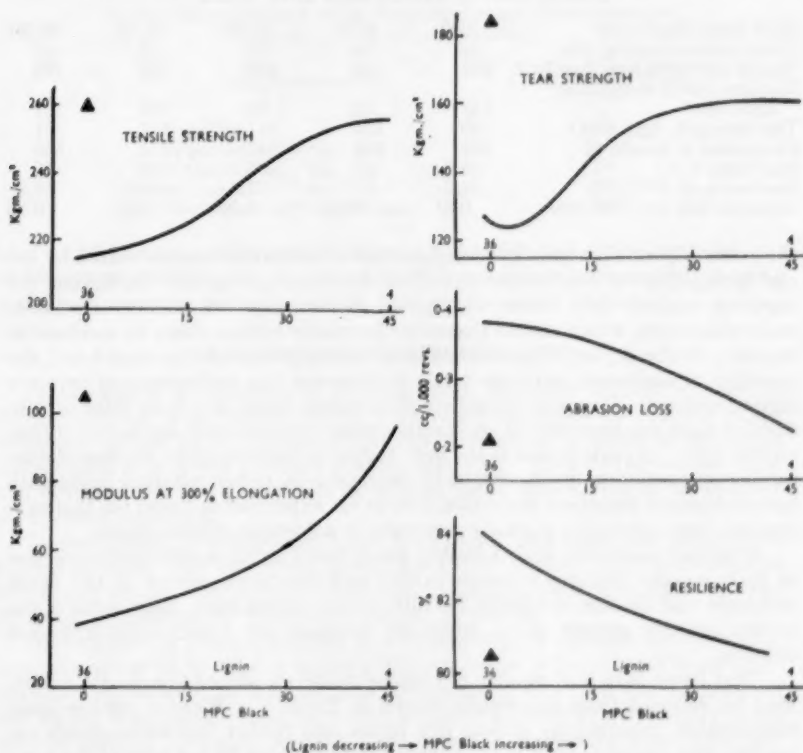
Fig. 2.—Effect of varying ratio of lignin to MPC black with constant loading (27.8 vols. phr). Composition: Rubber, 100; zinc oxide, 10; stearic acid, 4; M.B.T., 1; T.M.T.D., 0.1; sulfur, 3; lignin and black variable. ▲ denotes level of properties given by MPC black, 50 phr without lignin.

ings as high as 50 volumes of lignin and black, tear strength and resistance to abrasion are about the same as with 28 volumes of black alone. Resilience diminishes in proportion to the amount of black added to the lignin compound.

The results of the second series of experiments in which the volume of loading material was kept constant illustrate the possibility of achieving a compromise between high resilience and poor resistance to abrasion (Figure 2).

OTHER WAYS OF COMPOUNDING RUBBER WITH LIGNIN

When dry lignin, mechanically ground as finely as possible by normal methods, is incorporated into rubber by mill mixing the rubber is not reinforced, whereas when lignin and rubber are precipitated together from latex the resulting coprecipitate shows a degree of reinforcement comparable with that produced by carbon black. The cause of this disparity in behavior, due to a difference only in method of adding lignin to rubber, is not known. It may be supposed that when lignin is precipitated from solution in the absence of rubber

TABLE IV

COMBINATION OF LIGNIN WITH HAF BLACK

HAF black/lignin, phr	50/0	0/36	15/36	25/36	40/36
Total volume loading, phr	28	28	36	42	50
Tensile strength, kgm./cm.^{2}	204	216	202	193	170
Modulus 300% elongation, kgm./cm.^{2}	145	42	75	102	131
Tear strength, kgm./cm.^{2}	90	124	131	115	101
Elongation at break, %	388	648	547	473	388
Hardness, B.S.°	65	53	65	72	79
Resilience, at 70° C, %	69.3	81.1	72.0	64.0	58.5
Abrasion loss, cc./1000 revs.	0.21	0.48	0.39	0.33	0.25

the extremely small, highly hydrated particles first formed are prevented by the cushioning effect of their bound water from forming aggregates. On drying, the particles coalesce into coarse aggregates, bound together possibly by intermolecular forces, which cannot thereafter be readily broken down by mechanical means. In the drying of lignin-elastomer coprecipitates on the other hand, the presence of elastomer particles tends to obstruct the coalescence of primary lignin particles. Coprecipitates may thus retain lignin in a finer state of subdivision than can be achieved by incorporating dry powdered lignin into rubber on the mill. If particle size is the only factor in reinforcement, the loss of reinforcing properties on drying might be prevented by coprecipitating lignin with nonelastomeric dispersed materials, but so far experiments based on this supposition have been only partially successful in achieving reinforcement.

A further possibility is that freshly precipitated lignin is sufficiently reactive to form specific linkages between rubber and functional groups in the lignin molecule, and the loss of affinity for rubber that occurs when lignin dries is due to the reactive groups being internally satisfied, for instance by hydrogen bonding.

That lignin is in fact capable of forming relatively strong bonds with rubber may be deduced from the results shown in Table V. When a rubber-lignin masterbatch prepared by milling dry lignin into rubber was exhaustively extracted with aqueous sodium hydroxide solution about 29 per cent of the total lignin was extracted, whereas an unmasticated masterbatch of the same composition prepared by coprecipitation released nearly all the lignin into the

extractant liquid. Milling, however, rendered the lignin in the coprecipitate progressively less extractable until, after five minutes mastication on a cold mill, practically all the lignin was retained by the rubber. Possibly this is due to the destruction of the open structure of the unmilled coprecipitate making it less permeable to the extractant, but it is also possible that cold milling induces a rubber-lignin interaction which results in the bonding of lignin particles to rubber. The bonding occurs whether the lignin is incorporated by coprecipitation or by dry mixing, but seems to be greater in the former case.

REINFORCEMENT WITH DRY LIGNIN

The ideal solution of the problem of using lignin as a rubber reinforcing agent would be to prepare it in a dry active form suitable for compounding by conventional methods. If lignin were precipitated from solution in the presence of a protective material which would prevent the aggregation of the particles on drying, the reinforcing activity possessed by lignin when highly hydrated might be retained. Oils, soaps, higher alcohols, and resins were

TABLE V
LIGNIN EXTRACTABLE FROM RUBBER-LIGNIN COPRECIPITATE
(100:36) AFTER COLD MILLING

Milling treatment	Fraction of total lignin extracted with N NaOH
	%
Unmilled	90.5
10 passes, tight nip	67.8
20 passes, tight nip	17.9
40 passes, tight nip	1.8
Continuous milling, 5 mins.	0.6

tried as protective agents, without success. Aggregation of the particles was effectively suppressed only by adding such large amounts of protective agent that the mechanical properties of the final product were impaired.

EXPERIMENTS WITH HYDRATED LIGNIN

In the search for methods of utilizing lignin in rubber without recourse to the coprecipitation technique, several workers have reported that rubber can be reinforced by milling it with lignin that has been soaked in water or in a lignin solvent such as ethylene glycol or aqueous alkali[2,10]. Thus Soden[11] on one occasion obtained reinforced products by milling lignin into rubber as an aqueous gel in dilute ammonia.

In the present investigations it has been found that lignin and metal compounds of lignin that have been precipitated from solution by the addition of acid or salt are not only strongly hydrated, but are active in the sense that they reinforce natural rubber when incorporated by milling.

One method of preparing lignin in a hydrated form suitable for incorporation into rubber on the mill is to add a dilute solution of formic acid to an aqueous ammoniacal solution of lignin; the precipitate so formed is filtered, washed, and placed in a drying atmosphere until it contains about 40 parts of dry lignin per 100 parts of hydrated crumb. This material, containing more than half its weight of water, is a "dry", free flowing powder which can be milled into rubber without difficulty. The mixed lignin-rubber masterbatch is sheeted, dried to constant weight, compounded with vulcanizing ingredients, and cured.

TABLE VI

Physical Properties of Natural Rubber Compounded with Hydrated Lignin (Indulin A)

Precipitated with (1) formic acid, (2) ferric chloride, (3) lead nitrate, (4) potassium alum [loading, 36 phr calculated as dry lignin allowing for content of metal (Fe, Pb, Al) in the precipitate]

	(1) Acid-precipitated				(2) Fe-precipitated				(3) Pb-precipitated				(4) Al-precipitated			
Period of vulc. at 141° C, mins.	10	20	30	50	10	20	30	50	10	20	30	50	10	20	30	50
Modulus at 300% elong., kgm./cm.³	54	73	75	75	65	84	87	86	55	86	96	101	61	82	87	85
Tensile strength, kgm./cm.³	201	188	180	152	208	212	202	191	217	229	211	184	213	220	207	195
Elongation at break, %	611	514	500	455	592	526	504	493	616	530	492	437	616	546	525	506
Resilience at 70° C, %	83.8	88.0	86.8	—	78.7	82.8	80.8	—	82.9	85.7	87.9	87.7	79.3	81.9	82.2	—
Tear strength, kgm./cm.³		86				112				117				121		

Results obtained with hydrated lignin, prepared in this way or by precipitating lignin (Indulin A) by means of metal salts such as ferric chloride, lead nitrate, or potassium alum, are set out in Table VI. The physical properties of vulcanizates prepared from hydrated lignin are similar to those obtained with coprecipitates.

Hydrated lignin retains its reinforcing capacity on drying down to a water content of 33 per cent, calculated on the moist crumb. On further drying its activity falls sharply. Whether the change in the lignin is due to a loss of chemical reactivity at the critical moisture content, or to a progressive coalescence of the lignin particles into hard aggregates which fail to break down by shearing during mill mixing, is not known.

Table VII

COMPOUNDING WITH LIGNIN PASTES

Treatment	Optimum properties developed in standard test compound			
	Modulus kgm./cm.² at 300%	Tensile strength kgm./cm.²	Tear strength, kgm./cm.²	Resilience, %
(1) Dry powdered lignin (BDR)	42	146	52	75.9
(2) As (1) wetted with water	49	188	95	82.6
(3) As (1) wetted with 3% solution of ammonium laurate	49	202	110	82.0
(4) Lignin precipitated in presence of ammonium alginate, dry powder	28	137	—	79.3
(5) As (4) wetted with water	53	187	85	84.1
(6) As (4) wetted with 3% solution of ammonium laurate	57	196	87	83.9
(7) Coprecipitate (1:1)	41	205	121	83.8

LIGNIN PASTES

Reinforcing properties are also developed to an appreciable degree by lignin when it is pulverized and wetted with water. Straw lignin (BDR lignin) finely ground (95 per cent < 325 mesh) consists mainly of particles, or rather aggregates, of about 30 to 45 μ diameter. On wetting the powder with water the aggregates can be seen under the microscope to break down into smaller units.

Trials were made in which lignin powder was slurried with water or soap solution and homogenized by passing the slurry through a colloid mill. The slurry was then exposed to a drying atmosphere to reduce the moisture content uniformly from about 80 per cent to 40 to 60 per cent. The paste thus formed was incorporated into rubber by mill mixing, and the rubber-lignin masterbatch was dried, compounded, and vulcanized.

In another experiment lignin was precipitated from solution in the presence of a hydrophilic substance (ammonium alginate, 5 per cent calculated on the lignin) and the lignin was dried and then re-wetted with water. The purpose of the hydrophilic material was to facilitate re-wetting. The paste so obtained was incorporated into rubber as before. Table VII shows that with aqueous lignin pastes rubber compounds can be prepared with properties approaching those obtainable with lignin coprecipitates.

It should be noted, however, that the results in Table VII were obtained only with BDR straw lignin; when similar treatments were applied to Indulin A

and to HS oxidized lignin the physical properties of the vulcanizates were of a lower order.   The hemicelluloses in BDR lignin, by assisting the dispersion of aggregates, may be partly responsible for the good physical properties obtainable with BDR lignin slurries.

MASTERBATCHES FROM LATEX–LIGNIN SLURRIES

As there might be practical objections to compounding dry rubber with a hydrated material or an aqueous paste, consideration was given to the possibility of preparing dry masterbatches from mixtures of latex and powdered lignin.   Pulverized BDR lignin in the form of a 20 per cent aqueous slurry was colloid-milled and intimately mixed with ammonia-preserved rubber latex in the proportion of 3 parts rubber to 10 parts lignin.   Formic acid was added to reduce the pH to 4 and the flocculated mass was dried at 40° C.   This masterbatch, with a high ratio of lignin to rubber, was compounded by milling additional rubber and vulcanizing ingredients into the well premasticated masterbatch.   Table VIII illustrates the physical properties of standard test vul-

TABLE VIII
COMPOUNDING WITH MASTERBATCHES FROM LATEX–LIGNIN SLURRIES

	Time of optimum cure at 134° mins.	Optimum properties developed in standard test compound			
		Modulus, kgm./cm.² at 300%	Tensile strength, kgm./cm.²	Tear strength, kgm./cm.²	Resilience, %
(i) Masterbatch from lignin slurry with 60% latex	20	44	204	105	83.2
(ii) Masterbatch from lignin slurry with centrifuge skim latex	20	65	204	87	73.3
(iii) Coprecipitate (1:1)	30	41	205	121	83.8

canizates prepared in this way using (i) commercial 60 per cent latex concentrate, (ii) centrifuge skim latex and, for comparison, (iii) rubber-lignin coprecipitate (1:1).

The foregoing method of preparing rubber-lignin masterbatches would appear to have several advantages over the conventional coprecipitation technique.   For instance the use of caustic alkali to bring lignin into solution is avoided, and the consumption of acid is limited to the amount necessary to flocculate the latex.   Relatively small proportions of rubber in the masterbatch suffice to ensure the retention of reinforcing power in the lignin so that the production of masterbatches at the pulping plant, using preserved latex as the source of rubber, may be economically as attractive as transporting lignin to the rubber plantation and coprecipitating it with fresh latex.   With a rubber-lignin ratio of 3:10 the masterbatches require handling by a special technique to ensure good dispersion of lignin in the final compound, but it is possible that the ease of processing could be improved without loss of product quality by including suitable softeners in the masterbatch.

SYNOPSIS

The preparation and properties of natural rubber-lignin coprecipitates have been investigated.

Coprecipitates differing from one another in minor respects are obtained by varying the type of lignin, the ratio of lignin to rubber, and the conditions of coagulation and of compounding.   Rubber-lignin vulcanizates containing 28

volumes of lignin phr have high tensile and tear strength and high resilience. Inferior abrasion resistance, however, renders lignin unsuitable as a complete substitute for carbon black in a tire tread. Data are presented which demonstrate the possibility of replacing part of the carbon black in a tire tread by a considerably larger volume of lignin without serious loss of tensile or tear strength and with positive gain in resilience.

Besides coprecipitation with latex other methods of effectively incorporating lignin into rubber are described. Hydrated lignin, a freely flowing powder containing 35 to 60 per cent of moisture, can be incorporated into rubber to give compounds showing a similar degree of reinforcement to coprecipitates from latex. Finely ground dry lignin, superficially hydrated by wetting with water, also exhibits reinforcing activity. Masterbatches of high lignin content capable of giving good reinforcement have been prepared from latex and lignin slurries.

The loss of reinforcing activity of lignin on drying is discussed and the possibilities are considered of preparing lignin in a dry yet strongly reinforcing form which could be incorporated into rubber by conventional compounding methods.

ACKNOWLEDGMENT

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CONFERENCE DISCUSSION

Dr. NAUNTON recalled a visit he had made to the National Research Laboratories in Canada, in the course of which a rubber technologist had demonstrated to him some of the virtues of lignin-filled rubbers. He seemed, however, astonished when it was shown to him that the tear resistance of stretched lignin-filled rubbers was phenomenally bad.

Mrs. SAGAJLLO, replying, said that she had not encountered the phenomenon described by Dr. Naunton. Masterbatches prepared in London and in Malaya had in fact given good tear values whether the samples were prestretched or not. She had examined a few Canadian masterbatches and had found them generally good though rather variable; perhaps Dr. Naunton's observation was made on a sample that was not typical.

Dr. WAKE congratulated the authoress on the clear and excellent presentation of her paper and complimented her on being the only lady to present a paper in person before the Conference.

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NATURAL RUBBER COMPOUNDS FOR INTERMITTENT LOW TEMPERATURE SERVICE *

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INTRODUCTION

Modern trends in the field of transportation present the rubber industry with many formidable problems.   One of the foremost amongst these problems arises from the development of jet aircraft designed to operate in the substratosphere, and from the operation in Arctic regions of land vehicles and marine craft.   At such altitudes the exposed surfaces and working parts are subjected to extremely low temperatures yet it is essential that all materials used in such position should retain their characteristic properties.   In the case of rubber the problem is acute since the transition with decreasing temperature is from a highly elastic through a leathery to a rigid and brittle state; the increase in stiffness being by a factor of the order of 2×10^3.   The transition will be called the rubber to glass transition.   To each temperature corresponds a stiffness value which is attained immediately the temperature is established.   The present paper is concerned with the measurement of such characteristics of rubber and with methods of extending to lower temperatures the flexibility range of natural rubber vulcanizates.

It is recognized that another kind of transition takes place in rubber at low temperatures, namely a first order or crystalline transition and differs from the glass transition in requiring considerable time for its progress.   With well vulcanized rubbers not under high strain this time is of the order of months even at the most favorable temperature.   This second phenomenon is however important for the service behavior of rubber products and is the subject of other work by one of the present authors[1].   Although both phenomena lead to a stiffening of rubber at low temperatures it is important clearly to distinguish between them since radically different methods are needed to mitigate the two effects.   This clear distinction has not always been made in earlier work on rubber at low temperatures and this has caused some confusion.   In the present work the periods of exposure to low temperatures were insufficient to produce significant amounts of crystallization.

The conclusion to be drawn from published work is that of all commercially available organic elastomers natural rubber has the lowest rubber to glass transition temperature.   Other elastomers such as butadiene-acrylonitrile copolymers and GR-S having higher transition temperatures become glassy at temperatures where natural rubber is still serviceable and it is not therefore surprising that considerable research effort has been deployed in attempts to improve the low temperature performance of these synthetic rubbers[2].   These researches have resulted in significant improvements, in some cases by adjustment of the ratio of components in copolymers[3] but also by the employment of judiciously

chosen plasticizers with conventional synthetic rubbers[4,5]. Much less information on similar work with natural rubber can be found in the literature, possibly because service conditions have not until recently become sufficiently severe to approach the glass transition of natural rubber. However, it has been shown that improvement in the low temperature behavior of natural rubber can be achieved by plasticization[6,7].

EXPERIMENTAL METHOD

Relatively complete information on the frequency and temperature dependence of the dynamic properties of rubberlike materials may be obtained using known[8,9,10] experimental techniques. The measurements are, however, correspondingly protracted, and simple test methods have therefore been developed for the rapid evaluation of low temperature behavior. They involve, in one form[11,12], the measurement of the deformation (or residual stress) at a specified time after the imposition of a standard load (or deformation) a corresponding
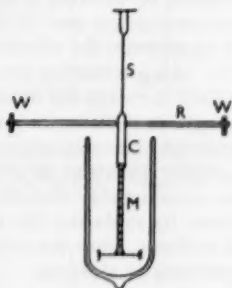
FIG. 1.—Simplified diagram of low temperature torsional pendulum apparatus.

value of modulus being calculated. Alternative instruments[13,14,15], based on the torsional pendulum, have the advantage of yielding separately the real and imaginary parts of the complex shear modulus, and the test method described below is of this form. A similar technique has been used by Nielsen[16] for the assessment of the structure of copolymers.

The apparatus is shown diagrammatically in Figure 1. It comprises essentially a torsion wire S gripped rigidly at its upper end and supporting at its lower end a carriage C holding a horizontal rod R, to the ends of which weights W may be attached. A long square-sectioned rubber prism M constitutes the testpiece, of length 8.0 cm. and side 0.375 cm., having metal endpieces bonded to it. It is held vertically with the upper endpiece fastened to the carriage, the lower endpiece being fastened to a metal plate which is comparatively flexible in a vertical sense, thus limiting the stress arising from differential thermal contraction of the rubber testpiece and the supporting frame, while being effectively rigid in torsion. The square cross section also mitigates the effect of small extensions on the measured properties[17].

The rod R is turned about the line of the torsion wire by an amount corresponding to a few per cent shear deformation of the rubber and then released, whereupon a damped torsional oscillation of the horizontal rod and carriage takes place, the period being governed by the total stiffness of the torsion wire and rubber prism and the moment of inertia of the moving parts, and the dec-

rement of vibrations being effectively governed by the hysteresis of the rubber. From experimental measurements of the period ρ and the logarithmic decrement δ of small torsional vibrations, obtained with a lamp and scale arrangement, and from the calculated moment of inertia I of the moving parts, the real and imaginary parts, n and $\eta\omega$ respectively, of a complex shear modulus of the rubber may be calculated:

$$n = A[4(\pi^2 + \delta^2)I/\rho^2 - s] \tag{1}$$

$$\eta\omega = A \cdot 8\pi\delta I/\rho^2 \tag{2}$$

s is the torsional stiffness of the torsion wire S, and A is given by the following relation for square-sectioned prisms of length l and side a:

$$A = 7.1 \, l/a^4 \tag{3}$$

The rubber prism and lower part of the carriage are placed inside a vacuum flask, the air inside which is cooled by blowing in spurts of liquid air, and circulated by a small fan. Thermocouples are used to detect temperature gradients within the vacuum flask, and to measure the effective rubber temperature to an estimated accuracy of $\pm 1°$ C. An alternative arrangement for measurements at greater than room temperature involves the circulation of heated air through the flask. As the rubber changes in stiffness on lowering the temperature, corresponding changes in the moment of inertia are made in order to maintain the period of vibration approximately constant at 2.5 ± 0.5 second. When the hysteresis of the rubber rises considerably the vibrating system may become "dead-beat". This is overcome by replacing the torsion wire by a stiffer one, and thus increasing the total stiffness, since the criterion for a dead-beat condition involves the ratio of hysteresis to stiffness.

CHARACTERISTICS OF THE LOW TEMPERATURE BEHAVIOR OF ELASTOMERS

Typical results for vulcanizates of varying polymers are given in graphical form in Figures 2 to 5. For several of these materials corresponding values were obtained by interpolation from the frequency and temperature dependence of the dynamic properties determined using the low frequency vibrator described elsewhere[9]. Good agreement was found.

Some general comments on the curves of Figures 2 to 5 may be made:

(i) The various polymers examined stiffen from a rubberlike to a glasslike state in the temperature range considered, while the imaginary part $\eta\omega$ of the complex shear modulus which is a measure of mechanical damping, passes through a pronounced maximum value at approximately the temperature at which a point of inflection is observed in the plot of log n against temperature. (In the case of the silicone polymer (Silastomer 181), however, where the transition is extremely abrupt, no comparable maximum has been observed.)

(ii) The real part n of the complex shear modulus which is the measure of the elastic stiffness appears to attain a limiting value in the glasslike state of approximately 10^{10} c.g.s. for all the polymers examined.

(iii) Variation in the degree of vulcanization over a wide range was found to influence slightly the position of the curves on the temperature scale, by two or three degrees, the shapes being substantially unaltered.
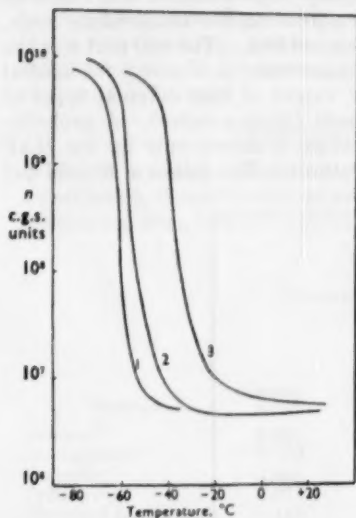
FIG. 2.—Elastic stiffness versus temperature for pure gum vulcanizates of: low styrene/butadiene copolymer (XPRD70), Curve *1*; natural rubber, Curve *2*; cold rubber (Krylene), Curve *3*.
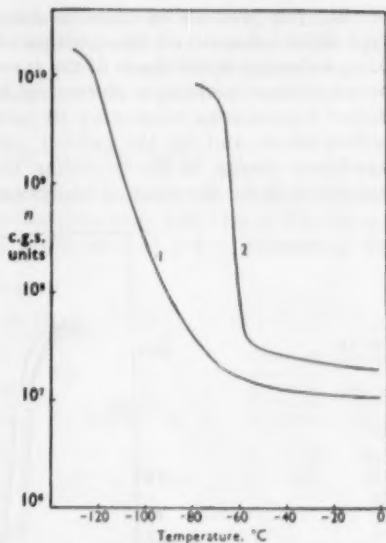
FIG. 3.—Elastic stiffness versus temperature for silicone rubbers: Silastomer 261, Curve *1*; Silastomer 181, Curve *2*.
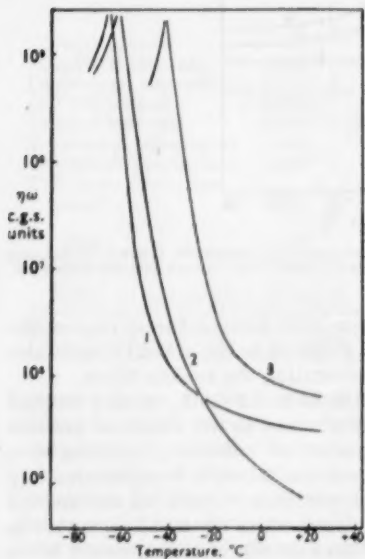
FIG. 4.—Hysteresis loss factor versus temperature for pure gum vulcanizates of: low styrene/butadiene copolymer (XPRD70), Curve *1*; natural rubber, Curve *2*; cold rubber (Krylene), Curve *3*.
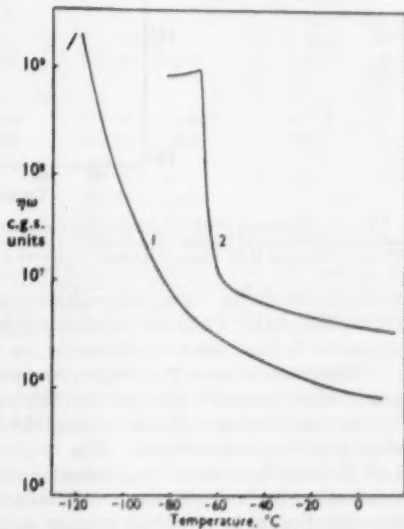
FIG. 5.—Hysteresis loss factor versus temperature for silicone rubbers: Silastomer 261, Curve *1*; Silastomer 181, Curve *2*.

(iv) The presence of fillers in comparatively large amounts was found to have little influence on the position of the curves on the temperature scale, though changes in the shape of the curves were evident. The real part n of the complex shear modulus is plotted against temperature in Figure 6 for natural rubber vulcanizates containing 50 parts by weight of four different types of carbon black, and for the unfilled vulcanizate (broken curve). A probably significant change in the transition temperature is shown only by the HAF compound in the direction of higher temperatures. The values of n (and $\eta\omega$)
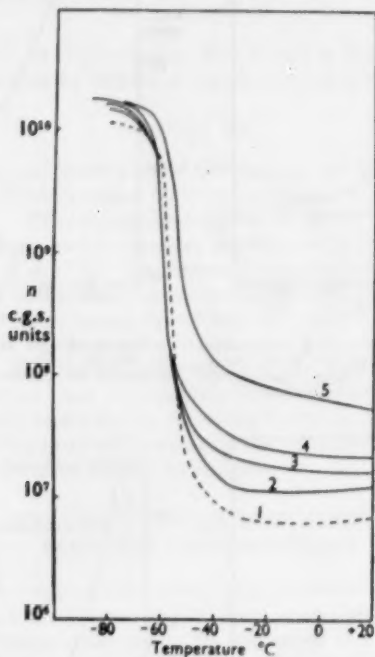
Fig. 6.—Variation of elastic stiffness with temperature for: pure gum vulcanizates, Curve 1; vulcanizates containing 50 parts MT black (Thermax), Curve 2; 50 parts FT black (P33), Curve 3; 50 parts lamp-black, Curve 4; 50 parts HAF black (Philblack O), Curve 5.

were found to be increased substantially at high temperatures, i.e., in the rubberlike state, while the level of modulus attained in the glasslike state also appeared to have risen significantly, on incorporating the various fillers.

Experiments over the frequency range 0.0052 to 5.2 c.p.s., using a method previously reported[9], showed that the curves of n and $\eta\omega$ are displaced towards higher temperatures on increasing the frequency of vibration, retaining substantially the same shapes. The displacement was found to be approximately 7.5° C for each factor of ten change in vibration frequency, for filled and unfilled natural rubber vulcanizates. A similar displacement of the n and $\eta\omega$ curves in the direction of lower temperatures and without change of shape, occurs when suitable swelling agents or plasticizers are incorporated. The effect is of similar magnitude whether the plasticizer be added during mixing prior to vulcanization, or subsequently by swelling. Thus, in characterizing to a first approximation

the effect of plasticizer upon the rubber to glass transition it is necessary only to record the depression of the temperature corresponding to some defined point of the transition, e.g., the temperature at which the stiffness is increased twofold or tenfold, or the temperature of the maximum value of loss factor ($\eta\omega$) at a fixed frequency.

EXAMINATION OF PLASTICIZERS

In the search for plasticizers to lower the transition temperature of rubber vulcanizates, it was found that only limited data were available in the literature concerning the physical properties of plasticizers at low temperatures while

TABLE I

PROPERTIES OF PLASTICIZERS

Plasticizer	Density, g./cc.	Reputed crystallization temp., °C	Reputed boiling point, °C	Observed glass (G) or crystal (C) transition temp., °C	Linear swelling of standard vulcanizate, %
Geraniol	0.881	−15	229	G, −100	24
Iso-digeranyl	0.832		177 at 16 mm.	G, −98	46
Triacetin*	1.161	−78	259		2*
Tributyrin*	1.035	−75	315		6*
Dimethyl phthalate*	1.189	+5.5	282		3*
Di-*n*-butyl phthalate*	1.046	−35	339		10*
Di-*n*-butyl adipate	0.964		169 at 17 mm.	C, −25	28
Di-*iso*-octyl adipate	0.930	< −70	205 at 4 mm.	G, −88	32
Di-"79" adipate	0.934			C, −25	36
Dinonyl adipate	0.920		235 at 5 mm.	G, −75 (very viscous, −35)	34
Didecyl adipate				G, −85	32
Di-*n*-butyl sebacate	0.940	−8	344	C, −14	32
Di-*iso*-octyl sebacate	0.920	−55	248 at 4 mm.	G, −81	36
Di-"79" sebacate	0.910			C, −9	36
Dinonyl sebacate	0.920	−28 to −32		C, −30	31
Tri-*n*-butyl phosphate*	0.980	< −80	177 at 27 mm.*	G, −112	16
Tri-*iso*-octyl phosphate	0.926	−80	220 at 5 mm.	G, −83	28
Tributoxy ethyl phosphate*	1.016		223 to 230 at 15 mm.	G, −82	8*
TP.90B	0.970		196 at 5 mm.	C, −31	14
Silester 12	0.887		270 at 17 mm.	G, −120	35

NOTES: (1) *Iso*-octyl esters are from the 2-ethyl hexyl isomer of the alcohol. (2) "79" esters are from mixed normal primary and α-methyl substituted primary aliphatic alcohols in the range C₇ to C₉ with some saturated cyclic alcohols. (3) Nonyl esters are from 3,5,5,trimethyl hexanol. (4) TP.90B is a commercial high molecular weight polyether supplied by the Thiokol Corp., N. J., U.S.A. (5) Silester 12 is a long chain alkyl silicate supplied by Monsanto Chemicals Ltd., London.

practically no information at all existed on compatibility with natural rubber. Many materials were therefore examined for these properties and Table I gives details of the results obtained. Compatibility was assessed by determining the equilibrium linear swelling of a pure gum vulcanizate immersed in the liquid at 21° C ± 1°. It was assumed that equilibrium had been attained when no further change in length was detectable over a period of 24 hours; the test vulcanizate underwent a swelling in benzene indicating a molecular weight between crosslinks of 4.4×10^3. On lowering the temperature, many of the liquids increased in viscosity, finally setting to glasslike solids, without crystallization occurring. In other cases a crystalline solid was formed quite sharply

at a well defined temperature. The polyether TP.90B showed a pronounced tendency to supercool, being a comparatively stable liquid at $-55°$ C with a crystal melting point of $-31°$ C.

Some of the substances detailed in Table I must be considered impracticable, as they are either excessively volatile at ambient temperatures or inadequately compatible with natural rubber. Such rejected plasticizers are marked with an asterisk and the offending property is indicated also. However, a certain number of materials, particularly the higher esters, are not similarly disqualified and they were therefore examined in pure gum vulcanizates containing 30 volumes of plasticizer added to the unvulcanized compound. Table II records

TABLE II

PHYSICAL AND LOW TEMPERATURE PROPERTIES OF PLASTICIZED NATURAL RUBBER VULCANIZATES BASE COMPOUND

Ingredients	Parts by weight
Smoked sheet	100
Zinc oxide	5
Stearic acid	1
Phenyl-2-naphthylamine	1
Sulfur	2.5
N-cyclohexyl benzothiazolyl-2-sulfenamide	0.8
Plasticizer	30 volumes

Physical properties at cure for maximum modulus 100%, 20 min. at 140° C

Plasticizer	Tensile strength, kg./cm.³	Elongation at break, %	Modulus 100% kg./cm.³	Modulus 300% kg./cm.³	Modulus 500% kg./cm.³	Modulus 700% kg./cm.³	Hardness B.S. degrees	$\Delta T'$ ° C
None	304	705	8	23	82	299	48	Nil
Geraniol	94	965	1	5	9	20	<30	7
Iso-digeranyl	83	945	–	4	10	22	<30	21
Butyl adipate	156	725	3	13	33	137	32	22
Octyl adipate	168	750	3	12	33	133	33	13
"79" adipate	148	713	3	12	35	146	32	14
Nonyl adipate	162	728	4	12	36	146	32	10
Decyl adipate	171	740	3	14	39	150	31	14
Butyl sebacate	150	723	3	12	35	142	32	7
Octyl sebacate	160	735	3	12	34	139	31	15
"79" sebacate	179	755	3	12	37	146	32	10
Nonyl sebacate	166	740	4	14	37	143	31	14
Octyl phosphate	129	733	3	10	26	111	<30	14
T.P.90B	161	760	–	12	29	127	30	16
Silester 12	110	875	3	8	15	42	<30	19

the physical properties of these vulcanizates. The low temperature properties obtained on the torsion pendulum apparatus are indicated in the table by the value of $\Delta T'$, the depression of the temperature of maximum loss ($\eta\omega$) from the unplasticized value.

It will be observed that the physical properties of the compounds containing aliphatic ester plasticizers are all very similar and are relatively independent of the ester composition. However, octyl phosphate gives slightly softer and weaker vulcanizates and this loss of physical properties is even more pronounced with geraniol, iso-digeranyl, and Silester 12.

Based on low temperature performance the three most efficient plasticizers are butyl adipate, iso-digeranyl, and Silester 12. However, butyl adipate and iso-digeranyl are found to have excessive volatility at curing temperatures, the

latter compound being in addition very expensive to prepare. Silester 12 undergoes some decomposition during vulcanization; this does not appear to be sufficient to prevent completely its low temperature plasticization of rubber, but results in volatile products which continue to come off even from the cooled vulcanizate. It has also been noticed that this decomposition phenomenon is much more rapid in compounds containing blacks and siliceous fillers. Next in order of efficiency is the polyether TP.90B; this is slightly more efficient than the ester types and is stable to vulcanization but its low compatibility with rubber places a rather low limit on the possible modification of low temperature characteristics. This polyether is somewhat water soluble, and it has been reported[4] that it is readily extracted from GR-S by water at a temperature of $28°$ C; caution in its employment is therefore necessary. Considering the long chain aliphatic esters there is little to choose between the octyl, "79" and decyl adipates and octyl and nonyl sebacates. All have adequate compatibility and sufficiently low volatility to withstand vulcanization temperatures without appreciable loss, the differences in low temperature efficiency are barely significant and final choice would depend mainly on availability and price. The inorganic acid ester octyl phosphate also appears a suitable low temperature plasticizer for natural rubber although the softening of the vulcanizate is more pronounced than with the aliphatic ester types. The $\Delta T'$ value for geraniol appears lower than would be consistent with the good low temperature behavior of the pure plasticizer; however reference to Table I indicates the somewhat volatile nature of geraniol and it is probable that its test compound in Table II loses plasticizer during vulcanization.

One fact which at first sight appears paradoxical, is that a plasticizer may confer flexibility to rubber at temperatures far below the freezing (crystallization) point of the pure plasticizer. Examples are butyl adipate (freezing point $-25°$ C), "79" adipate ($-25°$ C), butyl sebacate ($-14°$ C), "79" sebacate ($-9°$ C) and nonyl sebacate ($-30°$ C), all of which depress the glass transition of rubber below its normal value. This phenomenon is well known in the plasticization of polar polymers but so far does not appear to have been reported for natural rubber.

SELECTED PLASTICIZERS IN GUM COMPOUNDS

During the preparation of pure gum compositions on the open mill it was found that the addition of more than 30 volumes of plasticizer made handling very difficult due to the softening of the compound, while the addition of more than 40 volumes made mill mixing virtually impossible. However, by swelling the plasticizer into the raw rubber and compounding in an internal mixer in an atmosphere of nitrogen to reduce molecular degradation of the rubber[18] it was found possible to add over 70 volumes of a sufficiently compatible plasticizer, the resulting compound having no abnormal degree of surface tack and being sufficiently firm to permit further processing by normal methods. This procedure also gives some improvement in the physical properties of the final vulcanizate, as illustrated in Figure 7 for compounds containing octyl adipate, while the lowering of the transition temperature was found to be independent of the method of incorporation of the plasticizer.

The relation between the lowering of the transition temperature and concentration for Silester 12, iso-digeranyl, octyl adipate, and TP.90B is given in Figure 8. The latter two plasticizers were selected for more detailed examination because of their desirable physical properties and ready availability. The
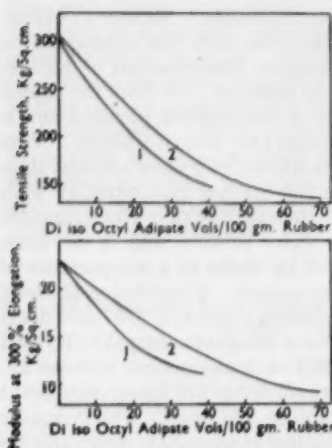
FIG. 7.—Effect of plasticizer content on physical properties of vulcanizate, compounds mixed in air, Curve *1*; in nitrogen, curve *2*.
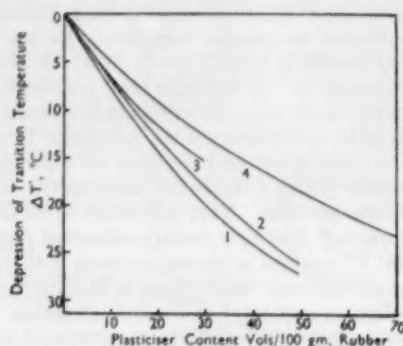
FIG. 8.—Effect of plasticizer content on transition temperature of pure gum vulcanizates; isodigeranyl, curve *1*; Silestor 12, Curve *2*; TP.90B, Curve *3*; di-iso-octyl adipate, Curve *4*.

polyether TP.90B is seen in Figure 8 to be the more efficient of the two as a low temperature plasticizer, while the physical properties of its vulcanizate appear from Table II to be equal to those given by use of octyl adipate. It therefore shows to advantage in producing intermediate low temperature performance, but its limited compatibility with natural rubber (about 30 volumes) restricts its use for extreme low temperature rubbers.

DEVELOPMENT OF PRACTICAL LOW TEMPERATURE RUBBERS BASED ON OCTYL ADIPATE

The use of suitable plasticizers for improving the behavior of natural rubber compounds at low temperatures has been demonstrated for gum compounds, but the development of materials which will give satisfactory performance

TABLE III

AGING OF NATURAL RUBBER GUM VULCANIZATES PLASTICIZED WITH OCTYL ADIPATE BASE MIX

Smoked sheet	100
Zinc oxide	5
Stearic acid	1
Phenyl-2-naphthylamine	1
Sulfur	2.5
N-cyclohexyl benzothiazolyl-2-sulfenamide	0.8
Octyl adipate	as indicated

	Per cent change after 7 days oven aging in air at 70° C			
Volumes of plasticizer	Tensile strength	Elongation at break	Modulus at 300%	Weight loss during aging
Nil	−11	−12	+32	0.3
10	−12	−14	+50	0.3
30	−55	−32	+33	0.3
50	−87	−57	+27	0.4
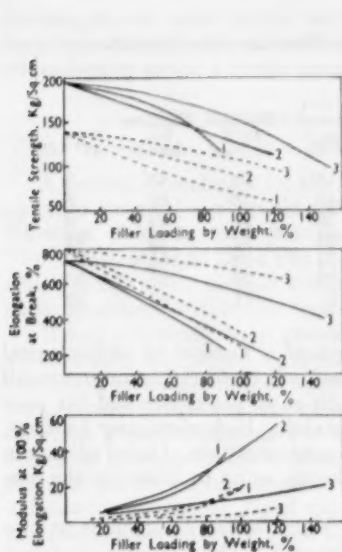
FIG. 9.—Physical properties of black compounds plasticized with di-*iso*-octyl adipate; 20 vols. plasticizer ———, 60 vols. plasticizer -----; HAF black, Curves *1*; lamp-black, Curves *2*; FT black, Curves *3*.
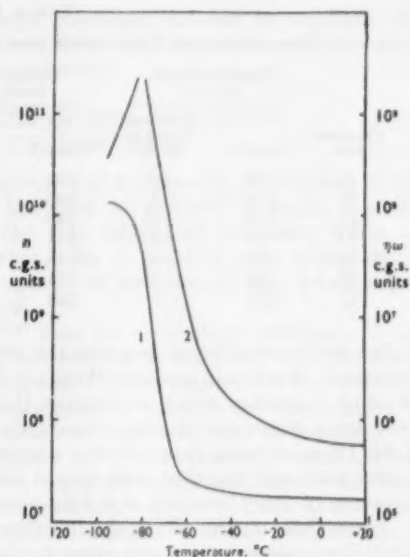
FIG. 10.—Low temperature behavior of typical natural rubber compound designed for arctic service (Compound G, Table IV); elastic stiffness, *n*, Curve *1*; hysteresis loss factor, *ηω*, Curve *2*.

TABLE IVA

LOW TEMPERATURE COMPOUNDS BASED ON PLASTICIZED NATURAL RUBBER

Depression of transition	B.S. hardness range		
	40–50	50–60	60–70
Approx. 8° C	Composition A	Composition B	Composition C
Approx. 20° C	Composition D	Composition E	Composition F
			Composition G

TABLE IVB

COMPOUNDING FORMULAS RELEVANT TO TABLE IVA

	A	B	C	D	E	F	G
Smoked sheet	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur	2.5	2.5	2.5 ·	2.5	2.5	2.5	3.5
N-cyclohexyl benzothiazolyl-2-sulfenamide	0.8	0.8	0.8	0.8	0.8	0.8	2.0
Hexamethylene tetramine	—	—	—	—	—	—	1.5
Phenyl-2-naphthylamine	1.0	1.0	—	1.0	1.0	1.0	1.0
Aldol α-naphthylamine	—	—	3.0	—	—	—	—
Octyl adipate	20.0	20.0	20.0	60.0	60.0	60.0	70.0
Silica (Durosil)	—	—	—	—	—	—	60.0
HAF Black (Philblack O)	—	—	70.0	—	—	120.0	—
Lampblack	40.0	75.0	—	80.0	100.0	—	—

TABLE IVc

PROPERTIES OF COMPOUNDS FOR LOW TEMPERATURE SERVICE

Composi-tion	Tensile strength, kg./cm.³		Elongation at break, %		Modulus 100% kg./cm.³	Hardness B.S. degrees	$\Delta T'$ ° C
	Unaged	% change 7 days at 70° C	Unaged	% change 7 days at 70° C			
A	169	−9	563	−13	11	48	8
B	141	−3	365	−19	26	60	8
C	171	−15	448	−23	21	63	8
D	97	−21	443	−24	11	42	21
E	82	−12	335	−24	19	55	20
F	66	−27	215	−16	27	66	20
G	121	−7	545	−2	11	63	22

under service conditions requires the solution of a number of technological problems. Foremost amongst these are the softening and reduction in overall physical properties which accompany the addition of plasticizer and the poor heat aging resistance of gum compounds containing high plasticizer loadings. Table III gives aging data covering a range of concentrations of octyl adipate in a pure gum mix together with weight loss during aging to illustrate the performance of this plasticizer in a vulcanizate.

Some data on the physical properties of black loaded compounds at two plasticizer concentrations are presented in Figure 9. The stiffening produced by even the highly reinforcing furnace blacks is not very pronounced, particularly at high plasticizer concentrations and as would be anticipated, very high black loading results in a large reduction in tensile properties.

Much more promising results have been obtained using the silica fillers, and composition G in Table IV illustrates the superior properties which may be obtained with such a filler in the presence of large amounts of plasticizer. It is noticeable that this compound has a higher value of hardness in comparison with 100 per cent modulus than is given by other fillers. Table IV gives compounds covering three hardness ranges and two levels of low temperature performance to indicate the order of physical properties which can be expected when using ester plasticized compositions. The problem of heat aging is by no means so acute in the presence of filler and in particular the compound based on silica shows satisfactory behavior in this respect. This compound with a hardness equivalent to a tire tread material remains flexible down to temperatures in the region of −80° C (see Figure 10). The only elastomers which can exceed this low temperature performance are certain of the silicone types and the physical properties of these latter materials, as currently available, are inferior to the compounds based on plasticized natural rubber.

The mixing of compounds containing large volumes of plasticizer together with filler generally presents no great problem since the plasticizer is readily absorbed by the filler and providing normal precautions are taken to prevent excessive breakdown, viz., use of even speed rolls and a wide nip except when grinding and of cool rolls to avoid sticking, little difficulty is experienced on an open mill. However, compounding in an internal mixer appears to be a more satisfactory method, particularly if the plasticizer is swollen into the rubber before mixing and the accelerators are added in the form of a well broken down masterbatch. In the case of silica type fillers the plasticizer and filler may be added together without prior swelling of the rubber since equal weights of silica and octyl adipate form a very stiff gel-like mixture which disperses readily.

In exceptional cases where very large plasticizer content is required, the technique of mixing in an internal mixer in an inert atmosphere affords some advantage in giving a firmer uncured compound.

THEORETICAL ASPECTS OF THE TRANSITION
OF A SWOLLEN ELASTOMER

A general formulation for the frequency and temperature dependence of the dynamic properties of an elastomer has been advanced[19,20] in terms of a distribution of elementary stiffnesses G_i; with associated relaxation times λ_i. The displacement of the n and $\eta\omega$ curves in the direction of lower temperatures which occurs when suitable swelling agents are incorporated may be appropriately considered within this framework.

It has previously been proposed[21,22] that the elementary stiffnesses G_i are substantially unchanged by swelling, except for a factor given by the volume fraction of elastomer in the swollen material. The reduction in a characteristic temperature for the rubber to glass transition, for example the temperature T' at which a maximum occurs in the $\eta\omega$ curve, must therefore be primarily ascribed to changes in the relaxation times λ_i. Furthermore the similarity in shape of the curves suggests that the values of the relaxation times at the characteristic temperature T'_s of the swollen state are equal to those at the characteristic temperature T'_u for the unswollen state. Such an identity would involve the equality of the flow viscosities at the respective temperatures. An isoviscous transition condition has previously been proposed[23] for more general application; within the restricted conditions here considered it does not seem implausible.

If a relation of the Arrhenius[24] form is assumed for the flow viscosity η' of a rubber-plasticizer mixture, i.e.,

$$\log \eta' = \nu_r \log \eta'_r + \nu_p \log \eta'_p \qquad (4)$$

where ν_r, ν_p are the volume fractions of rubber and plasticizer having flow viscosities of η'_r and η'_p, respectively, a particularly simple relation for the transition temperature T'_s in the swollen state may be obtained. The flow viscosities are assumed to obey temperature dependences of the form

$$\eta' = k \exp (Q/RT) \qquad (5)$$

over a limited temperature range, with apparent activation energies for viscous flow of Q_r, Q_p, respectively. Equating the viscosities of the mixture at a temperature T'_s and the rubber at a temperature T'_u, we obtain

$$Q_r/RT'_u = \nu_p \log (k_p/k_r) + (\nu_r Q_r + \nu_p Q_p)/RT'_s \qquad (6)$$

The first term on the right hand side of Equation (6) will in general be much smaller than the second, and on neglecting it, the following approximate relation is obtained for T'_s,

$$T'_s/T'_u = \nu_r + \nu_p Q_p/Q_i \qquad (7)$$

The coefficients Q_p of the temperature dependence of viscosity for three swelling agents have been determined using Ostwald and falling-ball viscometers over the relevant temperature range. The values obtained are given in

Figure 11 together with the theoretical curves of Equation (7) calculated from them using a value for Q_r of 23 kcal./g. mole. This value was chosen to give the best fit with the experimental data for octyl adipate. It is seen that Equation (7) predicts the linear relationship found in practice between T'_s/T'_u and ν_p for each plasticizer and that the position of the curves are also in reasonable agreement with experiment.

The validity of any relation of the Arrhenius type, Equation (4), for swollen long chain polymers is questionable, and its use in the present case is justified only by the reasonable agreement obtained. A critical experimental study of the flow viscosity of swollen polymers is necessary before a superior relation may be advanced, though crude measurements at room temperature of the viscosi-
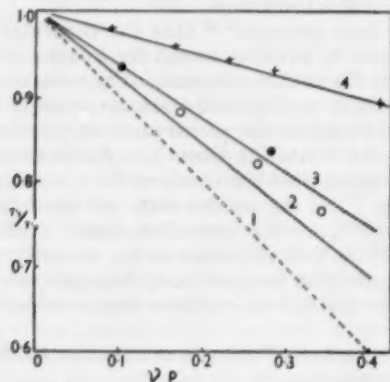
FIG. 11.—Effect of plasticizer volume fraction on transition temperature.

Plasticizer	Theoretical curve	Q_p kcal./g. mol.	Experimental
Ideal	1	0	
Dihydromyrcene	2	5	○
Iso-octyl acetate	3	8.5	●
Di-iso-octyl adipate	4	17	+

ties of mixtures of small amounts (of the order of 10 per cent) of liquid paraffin or octyl adipate with an oxidatively depolymerized rubber of about 20,000 mean molecular weight were in fair agreement with those predicted by Equation (4).

CONCLUSIONS

The changes in physical properties of rubber vulcanizates on approaching the so-called second order transition temperature are discussed and distinction is drawn between these phenomena and those associated with crystallization. A simple apparatus of the torsional pendulum type is used to determine the dynamic stiffness and hysteresis loss factor at a frequency of about 0.5 c.p.s. of vulcanizates in the temperature range 20 to −120° C. A large number of liquids are examined as potential plasticizers for lowering the rubber to glass transition temperature and a number are shown to have a high order of efficiency in this respect. Of these materials some also conform to the overriding requirements of low volatility and adequate compatibility with rubber. The loss in physical properties consequent on increase of plasticizer content is not markedly different for most of the plasticizers. Di-iso-octyl adipate is repre-

sentative of the liquids which give useful low temperature plasticization and a number of commercial type compounds are developed using this plasticizer with carbon black or silica reinforcement, some of these have transition temperatures approaching those of the silicone rubbers but with a better level of general physical properties.   A tentative theoretical treatment for the low temperature plasticization of nonpolar rubbers is discussed and this leads to a law which has been found to predict fairly well the transition temperature of a plasticized natural rubber compound in terms of the index of variation with temperature of the plasticizer viscosity.

SYNOPSIS

The provision of natural rubber compounds for service at very low temperatures requires the solution of two problems.   The first is concerned with the immediate changes in physical properties such as stiffness and hysteresis which occur when the temperature of the elastomer is lowered.   The second arises from slow changes in stiffness, associated with crystallization, which may be significant if the rubber is stored for long periods under strain at low temperatures.

This paper is concerned with the first problem and describes a simple test method based on the torsional pendulum which may be used to measure the stiffness and mechanical loss factor of a rubber compound at temperatures down to $-120°$ C and is capable of following the complete transition from the rubbery to the glassy state.   Rubber compounds may be characterized by a critical temperature, i.e., the temperature at which the stiffness is increased by a given factor (e.g., 2, 10, 100) with respect to the $20°$ C value, or by the temperature at which a maximum occurs in the loss factor vs. temperature plot.

In order to produce compounds having better overall low temperature performance than that exhibited by a simple compound of the same elastomer, suitable plasticizers are required.   Numerous materials have been examined and some are satisfactory in producing critical temperatures far below those shown by unplasticized natural rubber.   Special compounding techniques which prevent molecular degradation of the rubber have been developed. These allow the addition of the necessary quantity of plasticizer while maintaining a high standard of general physical properties.   Typical practical compounds of various hardnesses have low temperature characteristics approaching those of the special low temperature types of inorganic elastomers coupled with markedly superior physical properties.

ACKNOWLEDGMENTS

CONFERENCE DISCUSSION

DR. VAN ALPHEN said that in a rubber for use at low temperatures at least three things were necessary: the second order transition point must be low; the

rubber must not crystallize at low temperature; and the T-50 temperature must be sufficiently low. The third point could perhaps be solved by judicious choice of the method of vulcanization and the first had been solved by the authors by the addition of plasticizers. Were they not afraid that the mixing in of plasticizer enhanced the rate of crystallization at low temperatures as the molecules became more mobile?

MR. FLETCHER, in reply, said they had specifically excluded any discussion of crystallization. They were aware of some very interesting implications in the interaction of the two effects: it was quite possible that the rate of crystallization might be changed by the presence of plasticizers, but the data were not yet complete and would be published later.

DR. LETH PEDERSEN asked for a comparison between results obtained and those of the steady torsion test.

MR. FLETCHER said that in terms of the reduction in transition temperature by plasticizers the two tests would give equivalent results. The actual transition temperatures indicated by the two tests would differ somewhat because of the difference in the time factor.

DR. THIRION asked whether the authors had compared the dielectric and mechanical properties of some of the plasticized compounds as it might lead to interesting similarities between the effect of temperature on each kind of properties. For example, plasticization far below the crystallization point of the solvent had already been found by measuring the dielectric loss factor of natural rubber swollen in bromobenzene.

MR. FLETCHER, in reply, said that no such comparison had been made in the present work. Dr. Thirion's mention of a solvent addition made it relevant to say that one could achieve extremely low values of second order transition temperature by incorporating certain liquids; for example, rubbers plasticized with certain materials had retained flexibility down to $-120°$ C, but these were quite impracticable as plasticizers because of high volatility.

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THE REACTION OF MOLECULAR
OXYGEN WITH RUBBER *

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It is nearly a century since Hofmann and Spiller made the first recorded
experimental observations linking oxygen with substantial changes in polyiso-
prenoid hydrocarbons[1]. In the first sixty-odd years following this work tech-
nological progress was slow, but certain characteristic features of the oxidation
reaction were observed. It was firmly established that oxygen played an im-
portant role in the deterioration of rubber and rubber products with the passage
of time, and the accelerating effects of exposure to light or to elevated tempera-
tures were realized. Within a short additional period a very nearly complete
solution to the problems of oxygen aging was obtained with the discovery of
efficient vulcanization methods and of effective antioxidants. These dis-
coveries made possible the transition of rubber from a relatively expensive,
short-lived material of commerce to its present position of a high-volume, low-
cost, essential ingredient of our everyday life. Since that period technological
progress has consisted in steady refinements of these important discoveries.

During these years many observations necessary for understanding the
chemistry of the oxidation process were accumulated, but it was necessary to
wait for two fundamental developments in order to obtain a complete explana-
tion of the reactions occurring during the reaction of rubber with oxygen.
These were, first, a clear realization of the high molecular character of the rub-
ber hydrocarbon and the effect of this on its macroscopic properties, and
second, the work on oxidation of low molecular weight olefins which forms the
basis for inferring the nature of steps in the oxidation of rubber inaccessible
because of experimental difficulties. Since both of these developments have
been made it is quite probable that we shall know in complete detail the re-
action sequence in rubber oxidation before the centennial of Hofmann's paper
is reached.

In one sense this process is already completely understood. Considering a
piece of vulcanized rubber as an array of strings tied together at random by a
few knots, its properties can be quantitatively described with an error of 100
per cent or less, simply in terms of the average length of the strings and the
number of knots. In this view, oxygen is pictured as a somewhat unique set of
scissors which may cut the strings or add knots to the assembly, depending on
the properties of the strings. The discussion in this paper is concerned with
what may be called the organic chemistry of the cutting process, that is, the
actual series of steps leading to what is observed macroscopically as the effect
of scission. It will be restricted to natural rubber because it is the rubber
which has been studied the most and is the only one for which we have some
idea of the molecular processes occurring.

THE LOCI OF OXIDATION

In the aging of rubber products in service, two loci for attack by oxygen may be distinguished—crosslinks and the interlink chains.   The sites of crosslinkage are chemically quite distinct from the rest of the mass, whose properties may be expected to be identical with those of the uncured hydrocarbon.   The relative importance of these two is still not clear.

Considering first the interaction of oxygen with the hydrocarbon, without the complication of crosslinks, we may start from the familiar phenomenon illustrated in Figure 1, which is redrawn from data obtained by McGavack and Lundstedt[2].   The time required for a sample of USF rubber to reach ML4-65
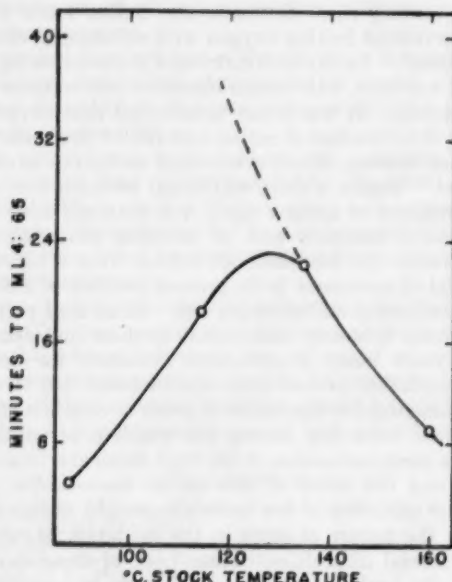
FIG. 1.—Rate of breakdown of USF rubber on an open mill.

when milled under standard conditions on an open mill is plotted against stock temperature.   The dashed line illustrates the behavior of rubber on oven aging at temperatures below the peak of the curve.   Over the entire temperature range covered by this curve oxygen is essential to the breakdown process[3].

On inspection of the curve it seems fairly obvious that the same reactions can hardly be involved at low temperatures as operate at high.   An explanation for the negative temperature coefficient of rate of breakdown indicated by the left hand portion of this curve was advanced by Kauzmann and Eyring[4] and thoroughly established experimentally by Watson and co-workers[5].   At low temperatures, where the viscosity of rubber is high, shearing stresses are high enough to cause rupture of the hydrocarbon.   The function of oxygen is to react rapidly with the free radicals formed by rupture, preventing their recombination.   Many other radical acceptors will function in the same way in low temperature milling, although none is as efficient as oxygen.

In contrast, the behavior indicated by the right hand portion of the curve of Figure 1 is unique to oxygen and exhibits the characteristic features of olefin oxidation in general.   It is this region which is pertinent to the problem of aging as well as to breakdown of raw polymer.

It is of some interest to consider for a moment the magnitude of the molecular effects which must be detected in investigating oxidation.   Figure 2 shows approximately the molecular weight of natural rubber as a function of its Mooney viscosity.   This curve is calculated from a large number of measurements relating solution viscosity and Mooney viscosity obtained by Lundstedt and Bevilacqua[6], using the relations given by Carter, Scott, and Magat[7], between solution viscosity and molecular weight.   The Mooney-solution viscosity data are in good agreement with one of the two published curves[8] relating
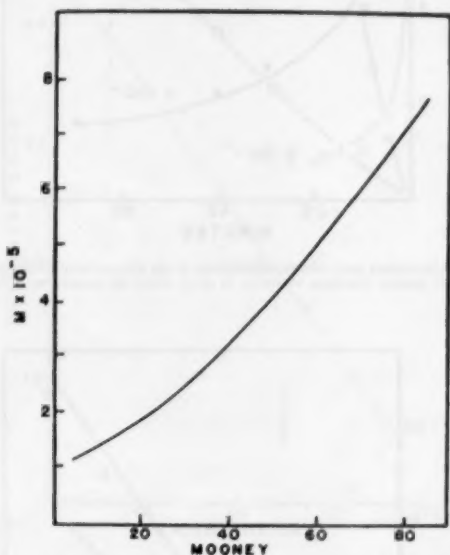
FIG. 2.—Relation between molecular weight and Mooney viscosity (natural rubber.)

these two.   In the range of Mooney viscosities encountered in practice, the molecular weight varies from the order of one million down to about one hundred thousand.   The concentration of free ends produced on breakdown is thus roughly 10^{-5} moles per gram.   In this paper quantities of oxygen absorbed and products formed are reported in units of this size, i.e., moles per hundred thousand grams.

The most obvious effect of the reaction of oxygen with rubber is the rapid fall in polymer viscosity produced by absorption of a small weight per cent of oxygen.   This is shown in Figure 3, which gives details for two experiments previously reported in part[9].   Oxygen consumed and intrinsic viscosity in benzene are plotted as a function of time at two temperatures in an atmosphere of oxygen.   The results illustrate both the rapid fall in rubber viscosity and the characteristic "autoacceleration" of oxygen absorption.   The correlation between oxygen absorbed and molecular breakdown is made more obvious in
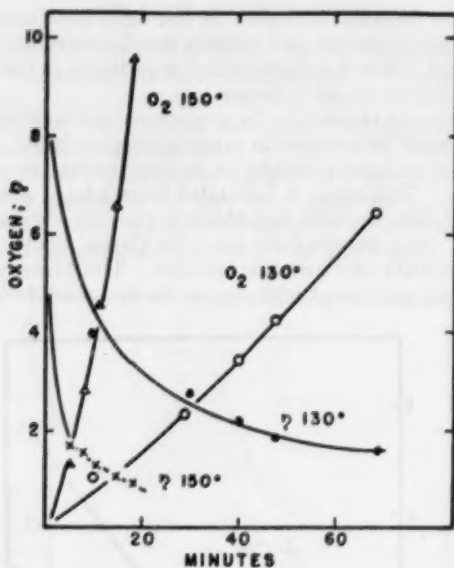
Fig. 3.—Oxygen absorption and rubber breakdown in an atmosphere of oxygen.   (Oxygen in moles per 10⁵ grams, intrinsic viscosity in dl/g; oven temperatures as indicated.)
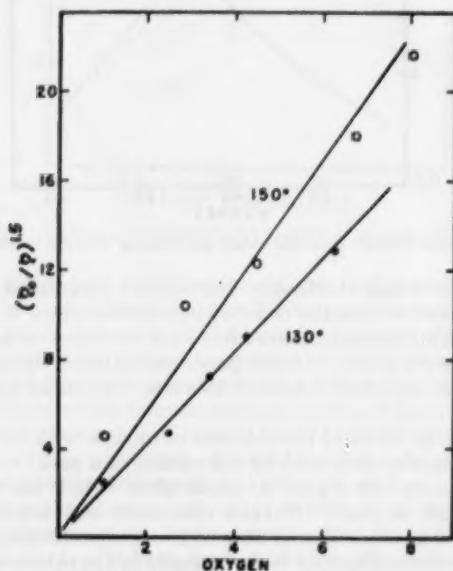
Fig. 4.—Correlation between oxygen absorbed and ratio of initial and final viscosities. (Oxygen in moles per 10⁵ grams.)

Figure 4. The quantity $(\eta_0/\eta)^{1.5}$ is very nearly proportional to the number of scissions of the hydrocarbon chain, so that it can be concluded that a constant fraction of oxygen consumed is used in scission.

This fraction is a function of temperature. The temperatures for the experiments illustrated in Figures 3 and 4 were chosen on the basis of observations by Tobolsky, Metz, and Mesrobian[10] which indicated that very efficient utilization of oxygen for scission occurs at high rates of oxidation (i.e., high temperatures), in contrast to low efficiencies observed by Farmer and Sundralingham[11] in work at room temperature. Although there is no quantitative
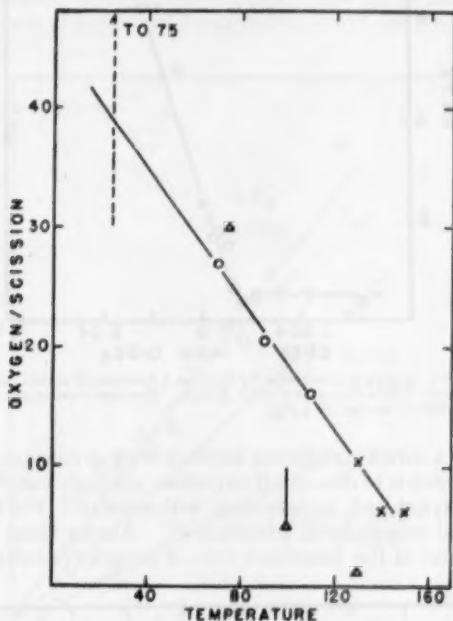
FIG. 5.—Scission efficiency as a function of temperature. (Moles oxygen/mole scissions.) Dotted line—Farmer and Sundralingham[12]; Vertical bar—Horikx[13]; Triangle—Tobolsky and others[10]; O—latex[14]; X—USF[9].

agreement between estimates of scission efficiencies obtained in various ways, they all agree with the conclusion of Tobolsky and coworkers that scission is more efficient at high temperature, as shown in Figure 5.

Figure 5 contains all the reported values of the relation between estimated oxygen consumption per scission and temperature, given with any supporting data, except those of Baxter, Potts, and Vodden[12] which are in general agreement with those of Tobolsky and others[10], which are plotted. The wide range indicated by the dashed line representing Farmer's results for photooxidation experiments[11] is not representative of experimental variation, but results from an apparent increase in oxygen required per scission as oxidation progresses. This was not observed in Bevilacqua's experiments. The triangles are taken from Tobolsky[10], the solid line from Horikx[12]; crosses represent experiments with dry raw rubber[9] and circles experiments with latex[14].
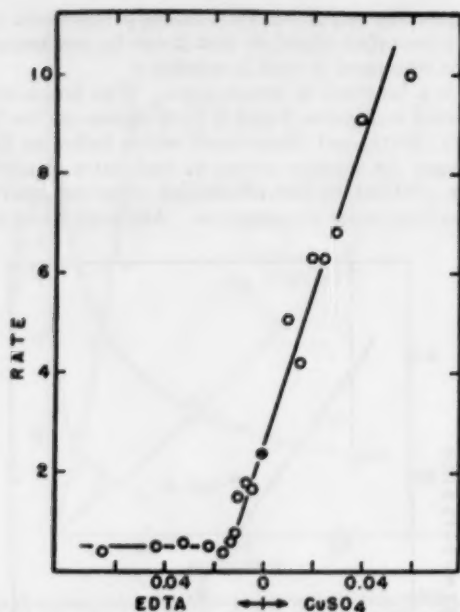
Fig. 6.—Constant rate of oxygen absorption by latex as a function of added inhibitor (EDTA, ethyl-enediaminetetra-acetic acid) or of accelerator (CuSO$_4$.5H$_2$O).   Abscissa—weight per cent copper equivalent to added material.   Ordinate—moles/10^3 g./hr.

Having found a direct correlation between oxygen consumed and molecular scission, the next step is to discover if any other products can be quantitatively correlated with oxygen and, by inference, with scission.   For this, oxidation of latex offers several experimental advantages[15].   Among these is the ready and reproducible control of the (constant) rate of oxygen consumption (Figure 6).
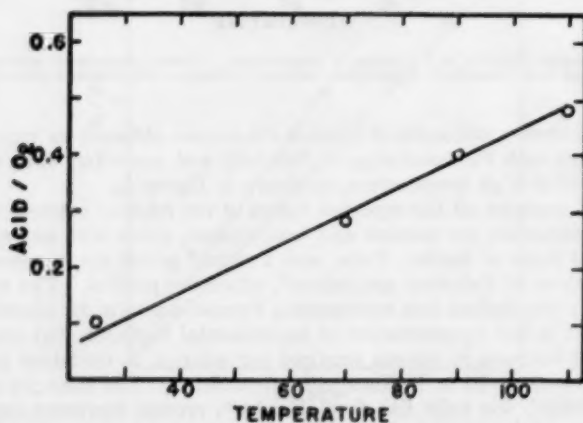
Fig. 7.—Titrable acid produced on oxidising latex.   (Acid/O$_2$ in equivalents per mole.)

It should be noted that the amount of EDTA required to reach the limiting rate is 50 to 100 times the amount equivalent to copper actually present in commercial latex.

The most important property of latex for our purposes is its reserve alkalinity, which traps acids effectively in the aqueous phase. Figure 7 shows that the yield of "total acid" determined by direct titration of the latex increases with temperature just as scission efficiency does (Figure 5). The only acids found to be formed on oxidation have been carbon dioxide and formic and acetic acids[15]. In Figure 8 the yields of these and of scissions of the hydrocarbon are plotted as a function of oxygen consumed. The curve labeled "acid" is the sum of the amounts of acetic and formic acids, which are produced in equivalent amounts[15].
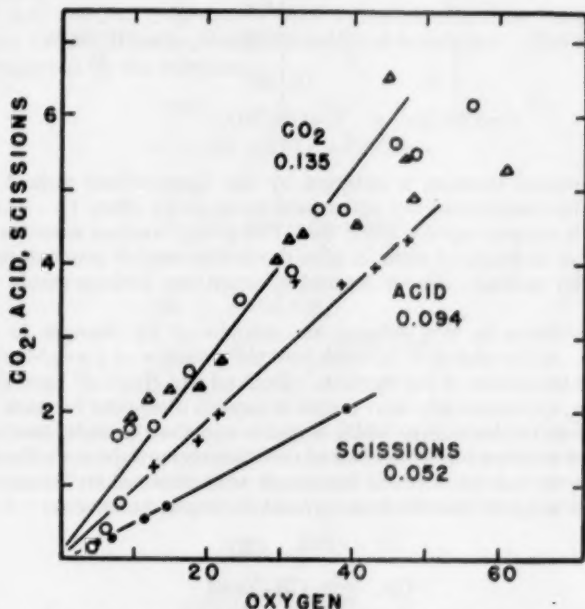
Fig. 8.—Products of the scission reaction at 90°. (Units: moles/10⁶ g.) Triangle—previously reported[14]; O—new data. (Numbers on curves are slopes in moles per mole.)

The data of Figure 8 were obtained from experiments at 90°. The ratios between CO_2, acids and scissions are independent of temperature[14]. Each of the quantities is a linear function of oxygen consumed, except that carbon dioxide appears to fall off at high extents of oxidation. This may result from exhausting the alkaline reserve. No loss of CO_2 has been observed on heating in nitrogen latex containing added sodium carbonate. Each curve in the figure is labeled with its slope. From these we can calculate the ratios:

$$\frac{CO_2/O_2}{Scissions/O_2} \approx 2.6$$

$$\frac{RCOOH/O_2}{Scissions/O_2} \approx 1.8$$

$$CO_2/RCOOH = 1.45$$

A preliminary carbon balance calculated from these figures shows that five or six carbon atoms appear as low molecular weight acids for each cut in the hydrocarbon chain, or approximately one isoprene repeating unit is destroyed at each scission.

To connect this rough stoichiometry with the details of the reactions which yield the observed products, it is profitable to review briefly what is known about olefin oxidation. The excellent kinetic work[16] done at the British Rubber Producers Research Association has established the reaction sequence outlined schematically below to describe the steps in the oxidation of simple olefins:

$$R\cdot + \quad \begin{matrix} \diagdown \\ \diagup \end{matrix}C=CHCH_2-$$

$$\downarrow (1)$$

$$\longrightarrow \begin{matrix} \diagdown \\ \diagup \end{matrix}C=CHCH-+ \quad \begin{matrix} \diagdown \\ \diagup \end{matrix}C=CHCOOH$$
$$H$$

$$\begin{matrix} \diagdown \\ \diagup \end{matrix}C=CHCH_2-+ \quad \begin{matrix} \diagdown \\ \diagup \end{matrix}C=CHCHO_2\cdot$$

(3) O_2 (2)
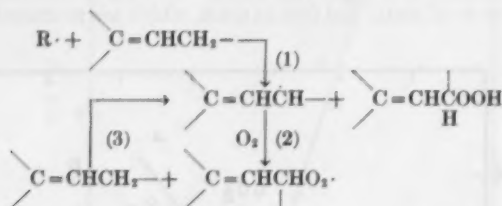
In this sequence reaction is initiated by the (unspecified) radical $R\cdot$ which removes a hydrogen from the alpha-methylene group (Step 1). The resulting radical adds oxygen rapidly (Step 2). The peroxy radical removes hydrogen from another molecule of olefin to give the hydroperoxide product and regenerate the allyl radical. Under favorable conditions hydroperoxide yields are very high.

Complications in this scheme are introduced by changes in the olefin structure. In the olefins of interest here the presence of a neighboring double bond alters the course of the reaction. Bolland and Hughes[17] have shown that, in squalene, approximately four atoms of oxygen disappear for each hydroperoxide (and active hydrogen) which appears and that on reduction of the peroxide a triol is formed in which two of the hydroxyl groups are adjacent. Several structures can be written, consistent with these observations. Bolland and Hughes suggest that the form present in largest amount is:

$$\begin{matrix} & & CH_3 \\ & & | \\ CH_3 & \cdot & CH_2COOH \\ | & & \\ -CH_2C=CHCH & & CHCH_2- \quad I \\ (1) & \diagdown & \diagup \\ & O\cdot O & \end{matrix}$$
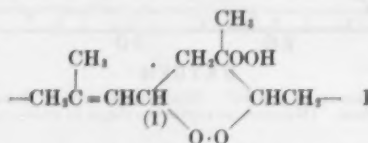
This is produced by the intervention of two additional steps in the sequence shown for simple olefins. The peroxy radical resulting from addition of oxygen at the carbon atom labeled (1) in the formula adds at one end of the nearby double bond to give a six-membered cyclic radical which then goes through the normal steps of oxygen addition and hydrogen capture.

Since squalene is structurally similar to rubber it is to be expected that similar forms exist in the oxidation products from rubber. The hydroperoxide as shown involves five carbon atoms and has a side chain methyl group which might appear in acetic acid, and thus might give rise to the observed products.

There is, however, one additional observation which cannot be explained on the basis of structure (I). It has been frequently observed[2,18] that a volatile

product is formed during the aging of rubber, which reacts with ammonia to form a product giving the color reactions of pyrroles. According to Whitby[19] it reacts with phenylhydrazine to give a dihydropyridazine identical with that obtained from levulinaldehyde:

$$OHCCH_2CH_2CCH_3$$
$$\overset{O}{}$$
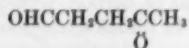
To form this from an intermediate involving the cyclic structure (I) shown above, carbon atom (1) would have to be reduced, an unlikely sequence of events.

However, this observation can be fitted into a consistent reaction scheme, derived from a hydroperoxide having the properties observed by Bolland and Hughes, if it is assumed that double bond shifts occur in that fraction of the intermediate oxidation product which is involved in scission. One such possibility is illustrated by the reactions:
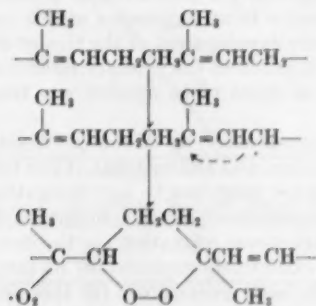
Without making any assumptions as to whether this peroxy radical or the hydroperoxide derived from it is the intermediate which undergoes scission in subsequent steps[20], it can be seen to contain all the structural elements required to account for known features of the reaction as shown in the following scheme:
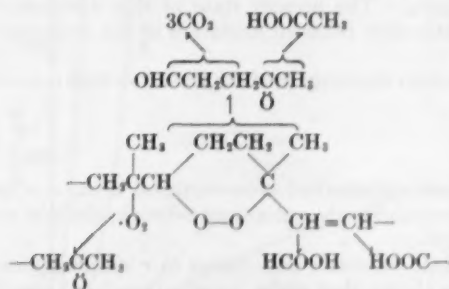
In summary these are:

1. Probable end groups on the oxidized hydrocarbon $CH_3C(O)$-and-CO_2H (Naylor[21]).

2. Levulinaldehyde production from dry rubber (Gorter[1] and Whitby[19]), in yields possibly approaching scission yields[18].

3. Formaldehyde and formic acid production (Kemp and others[22] and Dawson and Porritt[23]), in stoichiometric equivalence to scissions[15].

4. Stoichiometric acetic acid production[15].

5. Carbon dioxide/volatile acid ratio 1.5 (this paper).

6. Production of three moles of carbon dioxide and one of volatile acid per mole of levulinic acid oxidized in dilute ammonia solution[15].

7. Properties of the primary oxidation product of low molecular weight polyisoprenes (Bolland and Hughes[17]).

PROPERTIES OF CROSSLINKED NETWORKS

With this picture of the mechanism of the reactions leading to breakdown of the hydrocarbon itself set forth, we may turn to the alternative problem, mentioned in the introductory paragraphs, of what, if anything, happens at crosslinks when oxidation occurs.

New tools for investigating the properties of crosslinked networks are now in use in several laboratories in an aggressive attack on this problem. These tools have arisen out of the development of the theory of the macroscopic properties of a network as a function of the primary molecular size and of the crosslink density. The first of these to be applied was the phenomenon of stress relaxation.

It was observed independently by Mooney, Wolstenholme, and Villars[24] and by Tobolsky, Prettyman, and Dillon[25] that at low temperatures the stress in a piece of vulcanized rubber stretched to low elongations decreased relatively rapidly in an atmosphere containing oxygen, compared with the rate of decrease in its absence. Since then stress relaxation (or the closely related creep under constant load) has been extensively explored for its potential as an accelerated aging test, and is now in fairly general use for this purpose. It has two advantages over older tests: (1) it yields results very rapidly and is easily adapted to testing large numbers of samples[26] and (2) it measures a property which is probably closely related to the demands of some service conditions.

More recently, relaxation at constant strain has begun to be explored for its interesting possibilities for unraveling the fundamental molecular processes occurring during aging. The present state of this work emphasizes the importance of the distinction between oxidation of the hydrocarbon and of the crosslink.

The theory of rubber elasticity predicts a relation between stress and elongation of the form[27]:

$$\tau = RT\nu f(\alpha),$$

where τ = force/unit undisturbed cross-sectional area, ν = concentration of effective points of restraint in the vulcanized network, and α = ratio of stretched to unstretched length.

If T and α are held constant, any change in τ will be a measure of changes in ν. Bueche[28] has shown that under certain (assumed) conditions it will be possible to distinguish between random breaking of hydrocarbon chains and restricted attack at the crosslinks if either is the predominant way in which relaxation occurs. Figure 9 is taken from his paper. If scission occurs by a random breaking of hydrocarbon chains, stress decay with time should be of the form of Curve B. If only crosslinks are severed, Curve A represents the expected behavior. In practice, most observers have reported an approxi-
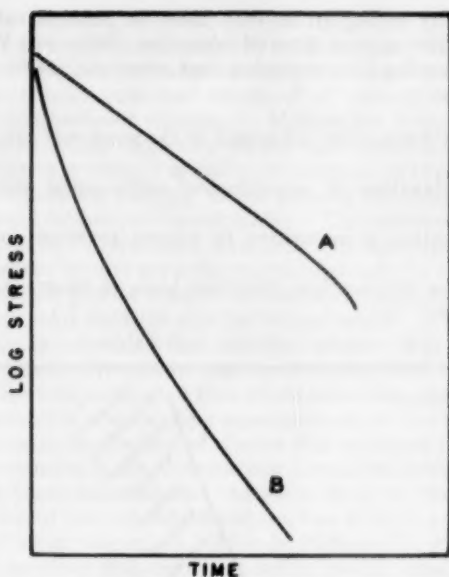
Fig. 9.—Stress as a function of time, calculated by Bueche[13]. Curve A—random scission; Curve B—scission restricted to crosslinks. Units arbitrary.
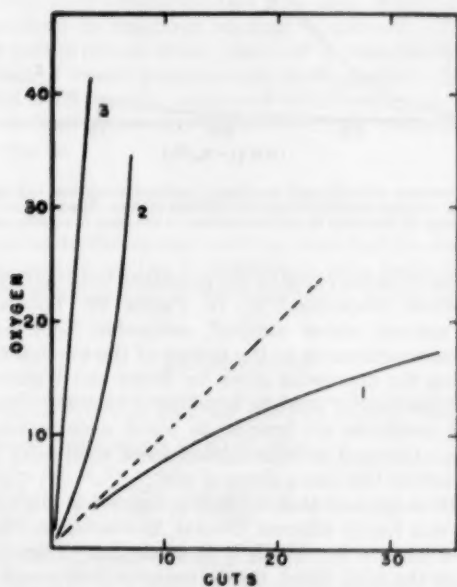
Fig. 10.—Oxygen required for scission in vulcanized rubber (see text). Units: moles/10⁶ g.

mately linear decay of log stress with time for natural rubber[10,12,26,29]. In addition to the evidence from rates of relaxation, Berry and Watson[29] list four other factors supporting the conclusion that crosslinks are broken in low temperature oxidation:

1. Different hydrocarbons vulcanized in the same way relax at comparable rates.

2. Rates of relaxation of peroxide and sulfur-cured natural rubber are different.

3. Stress relaxation is insensitive to oxygen pressure down to very low pressures.

4. Retarders for hydrocarbon oxidation have an unexpectedly small effect on relaxation rates.
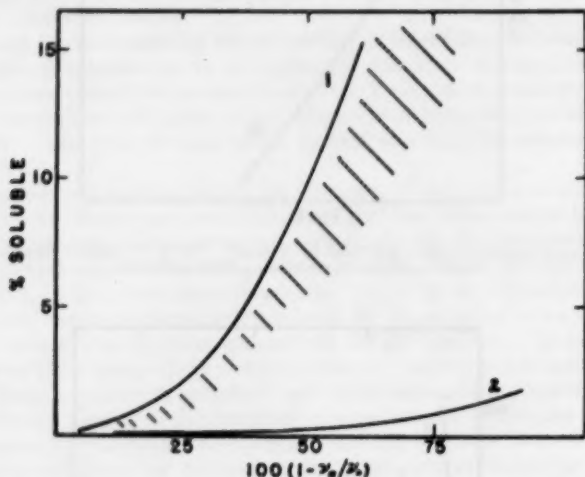
FIG. 11.—Relation between solubility and swelling of oxidized vulcanized rubber (schematic). Data from Horikx[14]. Curve 1—random scission; Curve 2—crosslink scission; Shaded area—experimental results. ν_e = effective concentration of crosslinks in oxidized rubber, ν_0 the same in starting material.

Another piece of evidence exists in the published information relating oxygen absorption and stress relaxation[10,12]. In Figure 10, Tobolsky's results for oxidation of one natural rubber sample[11], estimated from his Figure 11, are replotted for two assumptions as to the nature of the scission reaction. Curve 1 is calculated using the expression given by Berry and Watson[29] which relates residual stress and scission for random breaking of chains. Curve 2 is obtained by assuming only crosslinks are broken, in which event scissions are a linear function of stress. Curve 3 is interpolated from results for raw rubber (cf. Figure 5). The dashed line has a slope of one.

From Figure 10 it appears that if random scission is the only source of the stress decrease, it is a highly efficient process, increasing in efficiency as oxidation progresses—a process for which it is somewhat difficult to formulate a mechanism. If, on the other hand, breaks occur only at crosslinks, the amount of oxygen required for scission increases steadily as crosslinks disappear. This

is what would be expected, a priori, if both hydrocarbon and crosslinks are oxidized, but the latter react more rapidly with oxygen. It is consistent with the marked effect of combined sulfur on oxygen absorption rates.

Horikx[12] has recently published results of an alternative approach to the problem of estimating scission efficiency. Making use of expressions developed by Charlesby which relate molecular weight and crosslink density with solubility and swelling in a solvent of three dimensional networks, he has shown that the relation between swelling of the gel and the soluble fraction of an oxidized vulcanized rubber can be calculated. The relation is quite different, if scission is restricted to crosslinks, from that existing if random scission predominates. Horkix's results are redrawn schematically in Figure 11, in which the solid curve 1 is the predicted curve for random scission, curve 2 for crosslink scission. Experimental data for a sulfur vulcanizate lie in the shaded region. From this it may be concluded that crosslink scission, if it occurs, is a minor significance compared with random cutting of the hydrocarbon.

Although it has been suggested that stress relaxation does not measure the same thing as solubility and swelling measurements, it is not yet necessary to invoke a difference in mechanism to resolve this apparent paradox. There is no question that scission of the hydrocarbon does occur during oxidation at the temperatures of these experiments. At least three of the volatile products found on oxidation of raw rubber—water, carbon dioxide, and levulinaldehyde—are also found when vulcanized rubber is oxidized[1,18]. On the other hand, there is also no question that combined sulfur greatly accelerates oxygen absorption. The yield of levulinaldehyde is said to decrease with increasing combined sulfur[20] and the ratio of CO_2 produced to oxygen absorbed is less in vulcanized than in raw rubber[18].

Taken together, these results indicate that both crosslinks and the chains[31] between are involved in reactions leading to scission. The mechanism of chain scission at points remote from crosslinks is presumably the same as that in raw rubber; that at crosslinks remains to be elucidated. Horikx has pointed out that his results are equally consistent with scission at random and with scission at (but not of) crosslinks, which appears a reasonable interpretation of the available results.

ACKNOWLEDGMENT

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CHEMICAL REACTIONS OF ANTIOXIDANTS USED IN VULCANIZED RUBBER *

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Considerable evidence has accumulated during recent years which shows that the action of gaseous oxygen on unsaturated and saturated organic compounds takes place via reactions in which free radicals participate. As shown by Hock[1], Criegee[2], and Farmer[3], the oxidation of simple mono-olefins yields hydroperoxides. Based on a detailed study of the structure of these hydroperoxides, it was proved by Farmer that the reaction of oxygen with the unsaturated compounds commences at the allyl position. At this site a free radical stabilized by resonance is formed by dehydrogenation, the activation energy of the reaction being at the same time considerably reduced. These results have been confirmed[4].

From the oxidation of such Δ 1.5-olefins as squalene, dihydromyrcene, and other polyisoprenes, it was shown that reaction products are formed in which only half of the oxygen absorbed is present as hydroperoxide. According to Bolland[5] the cyclic hydroperoxide

$$\begin{array}{c} OOH \\ | \\ -CH_2-\underset{|}{\overset{CH_3}{C}}=CH-CH \quad CH_2-C-CH_3 \\ \quad\quad\quad CH-CH_2- \\ O\text{---}O \end{array}$$
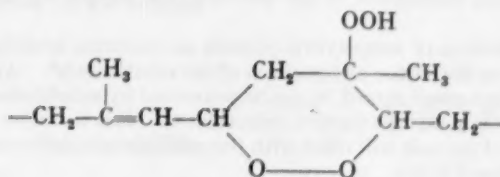
is formed by intramolecular bridge formation.

From kinetic study of the oxidation it is apparent that the initiation reaction is the formation of a free radical R· from the hydrocarbon RH and that the chain propagation reactions give the hydroperoxide molecule by direct addition of oxygen to R· under consecutive hydrogen abstraction from RH.

$$R\cdot + O_2 \longrightarrow ROO\cdot$$
$$ROO\cdot + RH \longrightarrow ROOH + R\cdot$$

Chain reactions such as the oxidation of olefins prove to be sensitive to inhibitors. Even small amounts of certain compounds inhibit the oxidation over a definite period of time. Especially, substituted phenols and secondary aromatic amines are important antioxidants in the rubber field.

Systematic experiments on the inhibition of the oxidation of ethyl linoleate initiated by the hydroperoxide of ethyl linoleate or by benzoyl peroxide shed considerable light on the mechanism of the action of phenols[6]. In accordance

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with this the chain stopping step arises from the reaction of the inhibitor (AH)

$$ROO\cdot + AH \longrightarrow ROOH + A\cdot$$

Efficient inhibitors are only such phenols which can be easily dehydrogenated but which are still stable to the action of oxygen. The oxidation-reduction potential is a qualitative measure of the energy required for dehydrogenation which is nearly a function of the type of substitution. The free radical A· should not continue the propagation of the chain but lose its activity completely by the formation of inactive products. It is the great number of possibilities offered by the aromatic nucleus for the formation of free radicals stabilized by resonance which makes the antioxidants originating from the aromatic series particularly effective. Further, secondary aromatic amines may react with the already formed hydroperoxides[7].

A structural change of the antioxidant occurs with these processes. The oxidation products are, however, very difficult to isolate because the antioxidant is used only in small quantities, the extraction from the high molecular weight compound being incomplete and the extracts being contaminated by other ingredients of the rubber mix.

It has been established, however, that with ethyl linoleate the initiation and also the propagation reactions do not differ whether the oxidation is initiated thermally, photochemically, or by the use of benzoyl peroxide[8]. It may thus be assumed that the reaction products derived from the reaction of the inhibitor with oxidizing agents are identical with the products formed during the inhibition of the oxidation of organic compounds. Several papers describe the oxidation products from antioxidants obtained with various oxidizing agents under conditions which correspond to the action of the oxygen on easily oxidizable materials.

The effectiveness of monohydric phenols as oxidation inhibitors depends to a large extent on the nature and position of the substituents[9]. Although phenol is active only to a small extent, it can be converted by substitution in the 2-, 4-, and 6-positions into highly effective antioxidants. It is therefore to be expected that substituted phenols will react with free radicals in a different manner from the nonsubstituted types.

Polyhydroxybenzenes, or the corresponding quinones, are formed from phenol by attack on the o- and p-position. With benzoyl peroxide[10] chiefly compound I is formed from p-cresol, whereas the substituted bisdioxydiphenyl II, in addition to a noncrystallizable tar, results from the reaction with ferric chloride[11] as well as with potassium persulfate[12], potassium ferricyanide[13] and Fenton's reagent[14], a mixture of hydrogen peroxide and ferrous sulfate. In the case of the two latter agents also the tetrahydrodibenzofurane derivative III could be isolated.

OCOC$_6$H$_5$ OH / OH (I)   OH   OH / CH$_3$ CH$_3$ (II)   CH$_3$ / O / CH$_3$ (III)
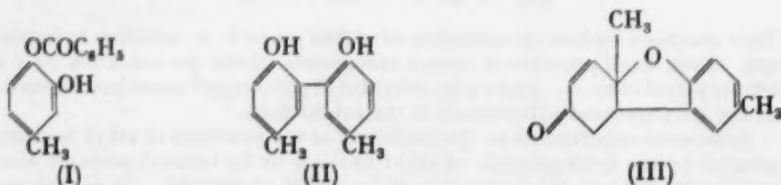
2,6-Substituted phenols are oxidized with a better yield to the corresponding diphenoquinones IV. The 3,3′,5,5′-tetramethoxy-4,4′-dibenzoquinone (IV,

$R = OCH_3$) is formed from 2,6-dimethoxybenzene and potassium dichromate[15] whereas IV ($R = C(CH_3)_3$) arises from 2,6-di-*tert*-butylphenol with a mixture of nitric and acetic acid[16].

$$R = CH_3, C(CH_3)_3, \text{ or } OCH_3$$

(IV)
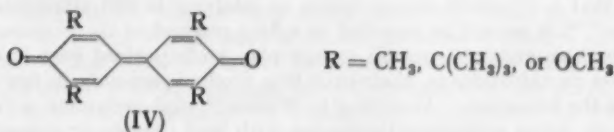
m-2-Xylenol gives with benzoyl peroxide[10] or with Fenton's reagent[14], in addition to the quinone IV ($R = CH_3$), small amounts of the corresponding dioxydiphenyl derivative V, whereas VI is formed from m-4-xylenol with benzoyl peroxide and VII with Fenton's reagent.

(V)   (VI)   (VII)
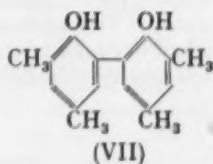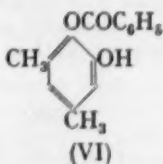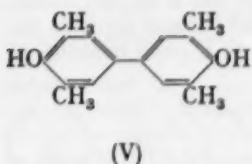
Although the reactive points in mesitol are blocked by substitution, the cyclohexadienone derivative VIII is formed in a good yield with benzoyl[10] or acetyl peroxide as well as with lead tetraacetate[17], in addition to a small quantity of the stilbene quinone IX ($R = CH_3$).

$R=CH_3$ or C_6H_5 $R=CH_3$ or $C(CH_3)_3$

(VIII)   (IX)
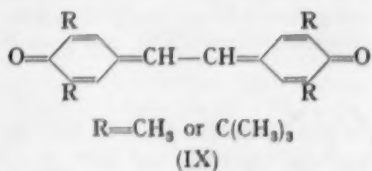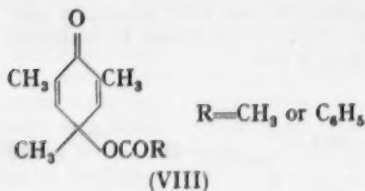
2,6-Di-*tert*-butyl-p-cresol is of considerable interest as a nondiscoloring antioxidant. Its oxidation with bromine[18], chromium trioxide[19], and potassium persulfate[20] leads to the aldehyde X. The corresponding cyclohexadienone derivative XI is formed as a main product in large quantities with *tert*-butylhydroperoxide[18] or with nitric acid[20]. Benzoyl peroxide[10] and lead dioxide[21] give the stilbene quinone IX ($R = C(CH_3)_3$) in addition to a small quantity of the corresponding phenol.

(X) $R=NO_2$ or $OOC(CH_3)_3$

(XI)
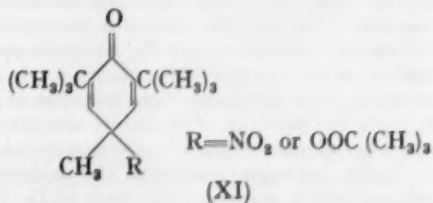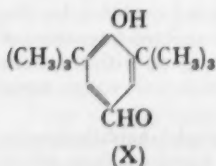
The presence of the stilbene quinone IX as an oxidation product of the 2,6-di-*tert*-butyl-*p*-cresol has been detected both in the inhibition of the oxidation of lubricating oils[21] as well as during oxidation of benzaldehyde[22]. In view of the fact that a relatively strong action as inhibitor is still attributed to this compound[20,22], it cannot be regarded as a final product of the oxidation.

Although secondary aromatic amines play an important part in technical application as antioxidants, their oxidation products are only in few cases described in the literature. According to Wieland[23], diphenylamine, a very weak antioxidant, forms tetraphenylhydrazine with lead dioxide or potassium permanganate from which N,N'-diphenylbenzidine (XII) is produced by benzidine rearrangement in the presence of strong acids. The latter compound can also be obtained in a high yield by reduction of the violet colored, semiquinoid salt of the diphenylbenzidine quinone formed from diphenylamine and potassium dichromate[24], or manganese dioxide[25] in sulfuric acid. This compound is suitable for the detection of small quantities of peroxides due to its easy oxidizability. Diphenylamine gives with acetyl peroxide and benzoyl peroxide the *o*-hydroxydiphenylamine derivative XIII in addition to a small quantity of tetraphenylhydrazine[26].

(XII)   (XIII)   (XIV)
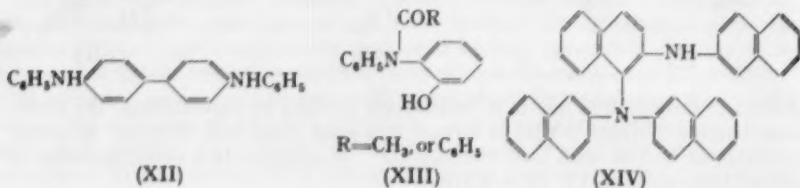
The semidine XIV[27] is formed from di-2-naphthylamine with potassium permanganate whereas phenyl-2-naphthylamine (PBNA), in addition to N-phenyl dibenzocarbazole (XV), also gives the semidine XVI[28].

(XV)   (XVI)   (XVII)
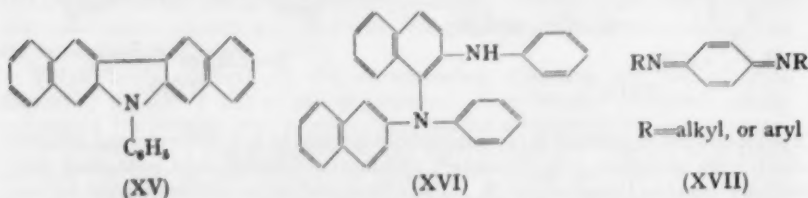
The presence of the latter compound could be proved by paper chromatography of the oxidation products formed during atmospheric aging of phenyl-2-naphthylamine-containing vulcanizates. Meyer[29], in a study of the oxidation products formed from phenyl-2-naphthylamine in synthetic rubber, claimed for semidine XVI the structure of a symmetric dinaphthyl diphenyl hydrazine. Rehner and coworkers supply, however, some constitutional evidence for the validity of the structural formula XVI. In addition, the expected quantities of methane are formed in the determination of active hydrogen, and with reactions to prove the presence of secondary aromatic amines characteristic colors occur which are characteristic of these compounds.

Under the same conditions the oxidation of the phenyl-1-naphthylamine with potassium permanganate leads to the formation of a black tar from which

a crystallizable compound could not be isolated. It is probable that a thorough oxidation takes place in this case.

The derivatives of p-phenylenediamine, which are particularly effective antiflexcracking agents, can be very easily oxidized. Thus, oxidation with atmospheric oxygen in the presence of small quantities of alkali[30], and also in the presence of lead dioxide[31] as well as organic peroxides[32], leads to the correspondingly substituted and strongly colored quinone diimines XVII. These products can be easily prepared by conducting a current of air through a weakly alkaline solution of the p-phenylenediamine derivative in alcohol. The oxidation is nearly quantitative after a few hours.

The oxidation products of the diarylamines contain several aromatic nuclei and show a smaller solubility in hydrocarbons as compared with the starting materials. It was therefore to be expected that the oxidation products formed from these compounds during atmospheric aging concentrate on the surface of the vulcanizate. Slightly loaded vulcanizates containing 1 part phenyl-1- or phenyl-2-naphthylamine and 0.15 part thiuram disulfide have been exposed to weathering for a period of 8 months. The dark brown deposit formed on the surface could be mechanically removed from the vulcanizate after wetting with methanol. After evaporation of the methanol the residue was dissolved in ethylidene chloride, freed from an insoluble portion with high sulfur content by filtration and the brown-black solution evaporated again to dryness, the last stage of this operation being carried out in vacuo. The oxidation products formed from phenyl-2-naphthylamine are a brown powder. They were obtained in a quantity of 8 g. per sq. m. of weathered surface and showed a melting range of 76–122° C. By means of ultraviolet spectra the presence of approximately 14 per cent phenyl-2-naphthylamine was demonstrated. The oxidation products formed from phenyl-1-naphthylamine in an approximately equal amount possess, however, a considerably lower softening point, a feature which indicates a thorough oxidation of the reaction products. Mixtures of several reaction products are involved in both cases and among these quinones, or similar compounds, were recognized by the fact that iodine was formed when adding them to a water containing solution of potassium iodide in glacial acetic acid. It was possible to brighten considerably the dark colored solutions in glacial acetic acid after addition of a small quantity of water by reduction with zinc dust. These compounds have, however, not been examined in detail.

A far-reaching separation of the quinones from the benzoid compounds was effected by coupling with diazotized aniline. Diazotized 1-naphthylamine-3,5,7-trisulfonic acid was, however, more suitable for the subsequent paper chromatography. A solution of 2 g. of the oxidation products in a mixture of dioxan and glacial acetic acid containing a small amount of pyridine was quantitatively coupled with diazotized trisulfonic acid using 8-amino-1-naphthol-3,6-disulfonic acid as an indicator. The addition of a small quantity of water caused an almost complete precipitation of the unreacted components of the oxidation mixture. After filtration, the clear solution was slightly evaporated in vacuo. The corresponding azo dyestuffs from the unoxidized starting compounds and from the semidine XVI were obtained in the same manner. No water was added to these solutions, they were only slightly evaporated in vacuo.

Paper 602 h-p made by Schleicher and Schüll was used for chromatography, the various dyestuffs solutions being applied to this paper in drops until all starting points showed the same color intensity. The solutions of the dyestuffs

obtained from the vulcanizates required, as a rule, amounts exceeding by 10–15 times those of the dyestuff solutions from the pure compounds. A mixture of 10 parts of the oxidation products obtained from PBNA in the vulcanizate with 4 parts semidine XVI was treated in the same manner. A mixture of methanol-amyl alcohol-benzene-water (2:1:1:1) served as developing liquid and this mixture enabled a far-reaching separation within 10 to 12 hours.

Phenyl-2-naphthylamine leads to a uniform violet colored dyestuff while several other dyestuffs are formed from the semidine XVI due to the larger number of couplings possible. These are clearly represented both by the oxidation product from the vulcanizate as well as by its mixture with the semidine. The relevant R_f-values[33] are shown for comparison in the following table:

PBNA		Oxidized PBNA					
1		2		3		4	
		With KMnO₄		In vulcanizate		Mixture of 10 pts. 3 and 4 pts. 2	
R_f-value	Color	R_f-value	Color	R_f-value	Color	R_f-value	Color
		0.8	Pink	0.8	Pink	0.8	Pink
		0.12	Blue-violet in U.V. light	0.13	Blue-violet in U.V. light	0.13	Blue-violet in U.V. light
		0.41	Light orange	0.42	Light orange	0.43	Light orange
0.62	Violet			0.63	Violet	0.65	Violet
		0.68	Orange	0.69	Orange	0.69	Orange

The R_f-values show good conformity and the semidine XVI can thus be considered as a component of the oxidation products formed from phenyl-2-naphthylamine during the atmospheric aging of rubber. In view of the fact, however, that this compound can protect vulcanizates from the action of oxygen, even though to a far lesser extent than phenyl-2-naphthylamine, it can only be an intermediate product of the oxidation. Products of a dark brown color are thus quickly formed from XVI by the action of organic peroxides at slightly elevated temperatures and with other oxidizing agents after longer heating periods. The examination of these oxidation products is so far not yet completed.

The paper chromatographs of the dyestuffs produced from phenyl-1-naphthylamine after atmospheric aging show besides the violet color from the unchanged amine some spots with a distinct fluorescence in ultraviolet light not given by the starting material. These compounds, however, have not been identified because it has been impossible to isolate crystallized substances either from the oxidation products obtained by open air aging or from oxidation products of the amine and potassium permanganate.

The results obtained with phenyl-2-naphthylamine indicate that its reactivity as an inhibitor of the oxidation in the presence of easily oxidizable organic materials runs parallel with the reactivity towards oxidizing agents. This supports also the theory that the oxidation processes of organic compounds proceed via reactions involving active free radicals.

SUMMARY

The work of Farmer and other authors has shown that the oxidation of unsaturated polymers proceeds via primary formed hydroperoxides. The addition of antioxidants, including chiefly compounds of the class of the phenols

and secondary aromatic amines, makes it possible to delay to a great extent the chemical changes taking place in unsaturated compounds. The mechanism of the action of phenols in the oxidation has been explained by Bolland.

It is difficult to separate from the polymer the reaction products which are formed from the antioxidant by the dehydrogenating action of the polymeric hydroperoxide radical. In view of the fact, however, that the kinetics of oxidation in the presence of added peroxide corresponds to the autoxidation of the unsaturated compound, the reaction between phenols or secondary aromatic amines and organic or inorganic oxidation agents has been studied in detail by several workers.

Depending on type, position, and number of the substituents, different reaction products are formed from phenols. Diphenylamine reacts with manganese dioxide to form a mixture of N,N'-diphenylbenzidine and the corresponding quinonedianil. N,N,N'-tri-2-naphthyl-1,2-naphthylenediamine is formed from di-2-naphthylamine with potassium permanganate, whereas under similar conditions phenyl-2-naphthylamine forms N,N'-diphenyl-N-2-naphthyl-1,2-naphthylenediamine.

Starting from the deduction that the chemical reaction products of the antioxidants accumulate on the surface of the vulcanized rubber due to decreasing solubility, pure gum stocks of cured natural rubber containing diphenylamine, N-phenyl-1- and 2-naphthylamine have been exposed to atmospheric conditions for 8 months. The dark colored reaction products could be removed mechanically from the surface of the cured goods after wetting with methanol. After evaporation, the residue was taken up in ethylidene chloride and the resulting solution evaporated to dryness. Amorphous mixtures of brown colored compounds were isolated from the vulcanizate containing diphenylamine and N-phenyl-2-naphthylamine, the reaction products of the N-phenyl-2-napthylamine being obtained as a dark colored tar. In addition to other compounds, the presence of the N,N'-diphenyl-N-2-naphthyl-1,2-naphthylenediamine was proved by paper partition chromatography of the resulting azodyestuff obtained from the mixture of the reaction products from phenyl-2-naphthylamine by coupling with diazotized 1-aminonaphthalene trisulfonic acid. The presence of this compound had also been shown by the ultraviolet spectra. In the same manner, small quantities of the N,N'-diphenylbenzidine could be recognized from the corresponding azodyestuff formed from the reaction product of diphenylamine. Due to extensive oxidation, the presence of reaction products could not be proved in any appreciable quantity from the reaction mixture of the phenyl-1-naphthylamine.

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CARBOXYLIC RUBBERS FROM SCRAP VULCANIZED RUBBER *

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U. S. RUBBER RECLAIMING CO., INC., BUFFALO, N. Y.

Scrap vulcanized rubber has been used principally for the manufacture of reclaimed rubber, which exhibits properties inherent in the original polymers of the scrap. Little has been found in the literature on the utilization of scrap vulcanized rubber as a low-cost starting material for controlled polymer synthesis. In the present investigation scraps containing natural and Type S synthetic rubbers have been modified to produce chemically different polymers possessing properties not usually associated with the initial elastomers. The authors believe that reactions with vulcanized rubber are not usually the same as reactions with the raw polymers and in this work the physical means of accomplishing the reaction are different.

In 1938 Bacon and Farmer[2] reported that when masticated raw natural rubber and maleic anhydride were dissolved in a solvent and the solution was heated in the presence of benzoyl peroxide, the ingredients reacted, yielding a variety of tough, fibrous, or resinous products[6,21]. When vulcanized natural and Type S synthetic rubber scraps were reclaimed in a Reclaimator[8,9] (a specially designed extruder type plasticator, made by the U. S. Rubber Reclaiming Co., Inc.) in the presence of a critical concentration of certain activated unsaturated compounds, a reaction occurred between the unsaturated compound and the scrap vulcanized rubber. With maleic anhydride, the resulting product was a carboxylated and replasticized rubber. This elastomer exhibited vulcanizing versatility via the carboxyl groups—i.e., curing with bivalent metallic oxides, diamines, glycols, epoxy resins, and diisocyanates. The polarity imparted by the carboxyl groups and the degree of crosslinking of the polymer appear responsible for its oil resistance, a property not normally present in a tire reclaim. The blocking of the double bonds, either by reaction at the double bond or by steric hindrance, added to the good aging properties anticipated with nonsulfur vulcanizates.

CHARACTERIZATION OF ACTIVE INGREDIENT

Unsaturated compounds containing an electrophilic or electron-accepting group alpha to the double bond have been combined with vulcanized natural and Type S synthetic rubber scrap. This work is based on the utilization of such compounds, wherein the electrophilic group is a carboxyl group. The reaction products have a lower benzene extract and higher tensile strength, modulus, cured hardness, and torsional hysteresis when contrasted with the corresponding reclaims. The products also exhibit oil resistance and good aging properties.

TABLE I

PHYSICAL PROPERTIES OF TRUCK AND BUS PEEL SCRAP
CARBOXYLATED WITH MALEIC ANHYDRIDE

	Min.	Control	Maleic anhydride
Concn. of active ingredient		0	4.0
ML/212/3–1		44	54
Cure at 287° F[a]			
300% modulus, lb./sq. inch	25	530	1510
	35	610	1640
	45	640	1675
Tensile, lb./sq. inch	25	1100	2250
	35	1140	2300
	45	1140	2300
Elongation, %	25	440	520
	35	440	495
	45	425	490
Hardness, Shore A	25	37	63
	35	38	64
	45	38	65

[a] Test formula.

The maleic anhydride and vulcanized truck and bus peel scrap form a
product very different from the corresponding reclaim (control) containing no
maleic anhydride, data on which are shown in Table I. The following test
formula was used:

	Parts
Hydrocarbon	100.0
2-Mercaptobenzothiazole	0.5
DPG	0.2
Stearic acid	2.0
Sulfur	3.0
Zinc oxide	5.0

Various organic acids, unsaturated[10] and saturated, when used as reclaiming
agents in small quantities generally upgrade the final product. Use of larger
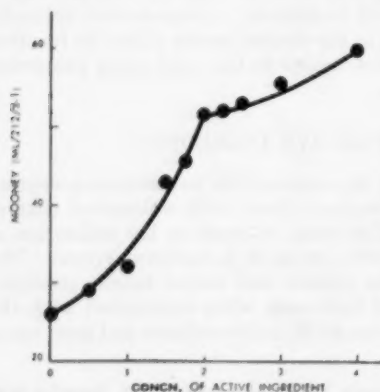
FIG. 1.—Relation of Mooney to concentration.
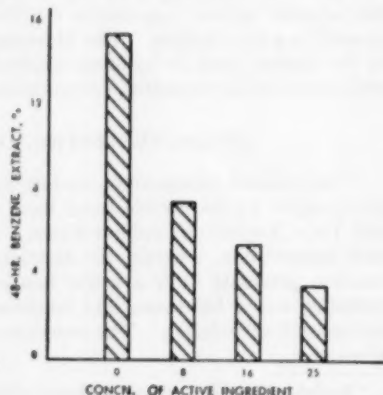
FIG. 2.—Relation of benzene extract to concentration.
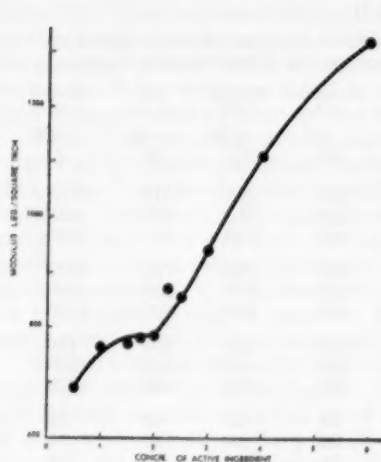
Fig. 3.—Relation of 300% modulus to concentration.
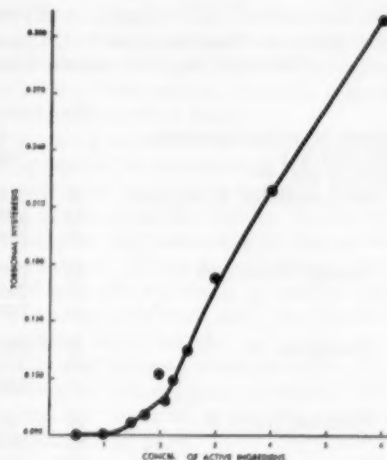
Fig. 4.—Relation of torsional hysteresis to concentration.

quantities of certain unsaturated acids, however, radically changes the characteristics of the polymer[17]. Comparative data on the effect of unsaturated and saturated acids are shown in Table II, where the effect of maleic anhydride is contrasted to that of succinic anhydride, which differs from maleic anhydride only in being saturated. The succinic anhydride produces a polymer of slightly higher tensile and elongation than the control, but otherwise similar in properties and characteristics. The polymer containing maleic anhydride, however, shows an anomalous increase in Mooney viscosity, modulus, and cured hardness. Further increase in concentration of the maleic anhydride shows corresponding changes in physical properties (Figures 1 to 4), in contrast to the changes ob-

TABLE II

RELATION OF UNSATURATED AND SATURATED ACID ACTIVE INGREDIENTS AS SHOWN BY PHYSICAL PROPERTIES OF PLASTICIZED RUBBERS

	Min.	Control	Maleic anhydride	Succinic anhydride
Concn. of active ingredient		0	4.0	4.0
ML/212/3–1		30	93	30
Cure at 287° F[a]				
300% modulus, lb./sq. inch	30	590	1060	690
	40	640	1150	695
	50	680	1250	720
Tensile, lb./sq. inch	30	820	1390	1200
	40	880	1420	1110
	50	940	1490	1120
Elongation, %	30	380	430	440
	40	380	390	420
	50	380	380	400
Hardness, Shore A	30	40	60	44
	40	41	61	45
	50	41	63	46

[a] Test formula.

TABLE III

PHYSICAL PROPERTIES OF VULCANIZED RUBBER SCRAP REPLASTICIZED IN
PRESENCE OF UNSATURATED COMPOUNDS vs. UNSATURATED ACIDS

	Min.	Control	Cinnamic acid	Styrene N-99	Iso-octene[a]	Fumaric acid
Concn. of active ingredient		0	6.2	4.25	4.6	4.8
ML/212/3-1		28	26	28	26	42
Cure at 287° F[b]						
300% modulus, lb./sq. inch	25	515	540	490	515	715
	35	570	650	545	600	880
	45	620	740	580	640	940
Tensile, lb./sq. inch	25	745	825	790	765	1020
	35	745	910	810	810	1090
	45	770	965	850	860	1160
Elongation, %	25	400	430	430	420	410
	35	370	400	410	380	380
	45	350	380	400	380	370
Hardness, Shore A	25	43	53	43	42	53
	35	44	54	44	43	54
	45	44	54	44	44	54

[a] Phillips Petroleum Co., Bartlesville, Okla.
[b] Test formula.

served with the succinic anhydride. The concentration of maleic anhydride used to prepare the sample shown in Table II is equivalent to that of the sample represented by concentration 4 in the figures. The effect of the unsaturated acid is therefore not attributed to the carboxyl or acid groups alone.

Comparative data on the effect of unsaturated compounds having an acid group alpha to the double bond and other unsaturated compounds are shown in

TABLE IV

EFFECT OF ACTIVE INGREDIENT ON PROPERTIES OF REPLASTICIZED
VULCANIZED SCRAP RUBBER

	Min.	Control	Maleic anhydride	Maleic acid	Citric acid	Fumaric acid	Itaconic acid	Aconitic acid	Cinnamic acid	Diethyl maleate	Dibutyl maleate
Concn. of active ingredient		0	4.0	4.8	8.0	4.75	5.3	7.1	6.1	7.0	9.3
ML/212/3-1		31	67[a]	70	44	67	42	45	42	29	24
Cured at 287° F[b]											
300% modulus, lb./sq. inch	30	510	1150	1065	1045	1015	760	830	730	530	355
	40	540	1320	1155	1190	1085	870	920	810	570	395
	50	525	1420	1215	1205	1195	990	985	860	595	420
Tensile, lb./sq. inch	30	770	1430	1460	1370	1310	1240	1410	1200	920	770
	40	905	1480	1555	1410	1330	1390	1460	1200	940	740
	50	900	1530	1565	1375	1375	1395	1430	1175	950	780
Elongation, %	30	390	390	425	400	390	450	475	440	440	470
	40	415	340	410	360	370	440	440	400	410	440
	50	410	330	390	350	340	410	410	370	410	430
Hardness, Shore A	30	37	58	53	50	53	47	46	54	39	33
	40	37	59	55	51	53	48	48	56	40	33
	50	37	61	55	52	53	50	50	58	40	34
Torsional hysteresis	40	0.099	0.179	—	—	0.114	0.100	0.100	0.162	—	—
48-hr. benzene extract, %[c]		15.6	12.3	—	12.7	12.0	12.8	—	—	—	—

[a] M/8212/3-1.
[b] Test formula.
[c] On uncured acetone-extracted sample.

Table III. Fresh styrene N-99 monomer (Dow Chemical Co., Midland, Mich.) was used both with and without inhibitor. The data obtained were essentially the same for the two; Table III shows the results obtained with the inhibitor removed. It has been concluded, in part from these results, that the general class of unsaturated compounds does not give the desired result.

Table IV shows the results obtained by using a series of unsaturated acids to give carboxylated elastomers exhibiting special characteristics common to the group. Mooney viscosities, moduli, and cured hardnesses are high as contrasted to the control. The initial reading obtained on the Mooney viscometer using the large rotor was above 200 for the maleic anhydride sample; hence the result reported was obtained using the small rotor. These materials have high torsional hysteresis[25]. The result obtained with the control is unusually high for this particular type of reclaim. Benzene extracts were made on uncured samples which had been extracted with acetone for 16 hours.

Table IV shows that citric acid imparts the physical characteristics of a carboxylic rubber to the elastomer. Citric acid, tribasic and saturated, does not meet the conditions for the active ingredient; however, at the temperature of the reaction it decomposes to give unsaturated acids. The literature[4,26] describes the decomposition of citric acid, whereby it loses water to form the unsaturated tribasic aconitic acid which may then lose carbon dioxide to form the unsaturated dibasic itaconic acid. These acids have the electrophilic carboxyl groups alpha to the unsaturation. Decomposition of the citric acid took place, as evidenced by the large evolution of gas during the reaction.

THEORETICAL CONSIDERATIONS

Bacon and Farmer[2] and Le Bras and Compagnon[22,23] had postulated that the reaction between maleic anhydride and masticated raw natural rubber was an addition at the double bonds of the rubber molecule. At a later date, however, Farmer[12,15] concluded that reactions between olefins or unconjugated polyolefins and maleic anhydride can be promoted at elevated temperatures, wherein the reaction is a substitution at the α-methylene groups of the olefin. Adler, Pascher, and Schmitz[1] have shown that the substitutive addition of maleic anhydride to simple olefins takes place at elevated temperatures. This reaction proceeds with particular ease in the system $-CH_2-CMe=CH-CH_2-$ of rubber. In the presence of benzoyl peroxide the rubber molecules are capable of forming free radicals at the α-methylene atoms. The radicals of rubber then add the maleic anhydride, the double bonds of which thereby disappear; the double bonds of rubber, however, remain intact[15].
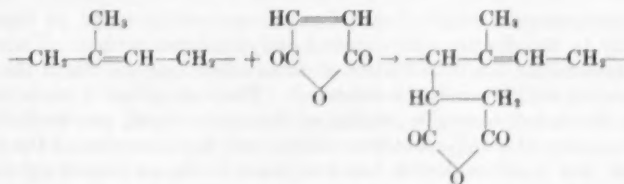
When rubber is masticated in the presence of air[11,15,19] at temperatures normally encountered in the Reclaimator[8,9,20], hydroperoxides, peroxides, and free radicals are formed mainly at the α-methylenic carbon and not at the double bond[12,14,29]. The initiating reaction may take place at the double bond. The

reaction between rubber and maleic anhydride should therefore proceed with ease in the present system in the absence of a free radical catalyst. This has been found to be the case; no difference was found, with or without the use of benzoyl peroxide.

Conceivably, an olefin may behave as either an electron donor or electron acceptor. However, olefins are predominantly electron donors, and natural rubber would be expected to be especially so, because of the inductive effect of the side methyl group. An electrophilic substituent—i.e., a substituent which

TABLE V

EFFECT OF MALEIC ANHYDRIDE AND CHLOROMALEIC ANHYDRIDE
ON PHYSICAL PROPERTIES

	Min.	Maleic anhydride	Chloro-maleic anhydride
Concn. of active ingredient		4.0	5.4
ML/212/3-1		88	85
Cure 287° F[a]			
300% modulus, lb./sq. inch	25	1150	1235
	35	1225	1350
	45	1260	1385
Tensile, lb./sq. inch	25	1375	1255
	35	1455	1350
	45	1450	1385
Elongation, %	25	390	305
	35	370	300
	45	360	300
Hardness, Shore A	25	58	61
	35	59	63
	45	61	63
Torsional hysteresis	35	0.234	0.298
48-hr. benzene extract, %[b]		12.3	8.3

[a] Test formula.
[b] On uncured acetone-extracted sample.

normally directs meta in the benzene ring—attached to the double bond of an unsaturated compound will withdraw electrons from the double bond.

$$\text{R—CH=CH} \rightarrow \text{COOH}$$
$$\delta +$$
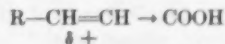
This electron-poor double bond of maleic anhydride would be expected to add readily to the electron-rich double bond of natural rubber. The reaction under consideration is a substitution at the α-methylene carbon of the rubber. This reasoning can, however, be extended. The assumption is made that substituents, which influence the polarity of the double bond, can similarly influence the polarity of an adjacent free radical, and the attraction of the negative radical for the positive double bond appears to be an important factor in facilitating this reaction[7,27].

The steric factor, also influences the reaction. Table IV contains data obtained by using a series of unsaturated acids and esters. Careful examination of the data, especially the 300 per cent modulus and the Shore A hardness, show that the reactivity of the active agent decreases from left to right. Thus maleic

anhydride is most active, but when the ring is open as in maleic acid or maleic esters, activity is greatly reduced.   Steric factors also appear to be responsible for the decreased activity observed when fumaric, itaconic, and cinnamic acids are used.   Chloromaleic anhydride appears to be slightly more active than maleic anhydride, as the former produces a polymer having a lower benzene extract and a slightly higher modulus, Shore A hardness, and torsional hysteresis (Table V).   This is explained by the electrical effect of the chlorine atom[7].

The carboxyl group of the unsaturated acid polarizes the π electrons in such a way that the beta carbon is positively charged.

$$R \overset{\beta}{\underset{+}{-CH}} \underset{-}{-CH} \to COOH$$
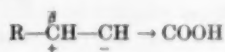
Because the free radical rubber is relatively negative, there is a strong electrical factor facilitating combination at the beta carbon of the acid.   For diethyl maleate not more than one carboxyl group at a time can be coplanar with the double bond due to steric hindrance:
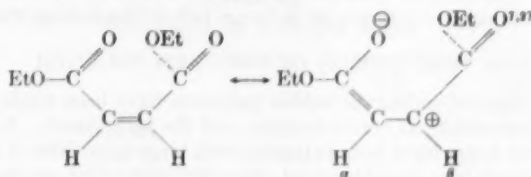
The reaction between the free radical and the double bond of the maleate is preferentially in the plane perpendicular to the atoms attached to the double bond, and, because the rubber radical is a "negative" radical, it should add preferably at the positive beta-carbon of the maleate[27].   As can be seen from the above formulation, there will be hindrance in this case which is not present in maleic anhydride or diethyl fumarate, which is the trans form[7,27,28].   Table IV shows the inactivity encountered with diethyl and dibutyl maleates.

METHOD OF PREPARATION

The reaction was accomplished in a Reclaimator[8,9], in which the ground vulcanized rubber scrap was subjected to heat, chemical action, and mechanical work.   The Reclaimator was heated to 325° F by means of oil jackets and the mechanical working raised the temperature of the material being processed to 400° to 450° F.   The screw was designed with special masticating sections to enhance the working and the intimate mixing of the ingredients.

The vulcanized polymer used was fabric-free whole tire or peel scraps ground to 30-mesh size.   The total rubbery hydrocarbon content of fabric-free whole tire scrap was about 55 per cent which consisted of approximately 50 per cent natural and 50 per cent Type S synthetic rubbers.   The peel scrap was considerably higher in natural rubber content, but it is considered that the butadiene units in the Type S synthetic scrap also take part in the reaction.   Analyses of typical scraps are shown in Table VI.

The ground vulcanized polymer and reclaiming ingredients were mixed in a pug mill-type mixer and the acid was added in crystal, flake, or powder according to the form available.   The reaction took place simultaneously with the

TABLE VI

TYPICAL ANALYSIS OF SCRAP USED

	Passenger whole tire	No. 1 truck and bus peels
Acetone extract	9.8	7.7
Ash	6.1	3.8
Carbon	25.4	28.4
Total rubber hydrocarbon	55.7	57.1
Direct rubber hydrocarbon (natural)	28.2	44.5
Difference (Type S synthetic)	27.5	12.6

reclaiming action.   The time of contact in the Reclaimator was the same as for the reclamation of the scrap rubber, about 3 minutes.   These reaction conditions were also used for the controls.

As the product was extruded, it was cooled immediately to prevent excessive oxidation.   The samples were then refined on a two-roll laboratory-size refiner and allowed to age a minimum of 24 hours before the testing was continued.

DESCRIPTION OF UNCURED POLYMER

Various types of carboxylic rubber polymers have been made, depending on the active ingredient, its concentration, and the scrap used.   In addition, the highly reacted types have been extended with large quantities of petroleum and ester oils.   Each type has its special characteristics which are developed to the fullest extent through proper compounding and processing.

As the concentration of active ingredient is increased upward from the critical point, a gradual transition may be observed from tough but still rubbery products (Figures 1, 3, and 4) to hard and brittle resins.   This progressive modification of physical properties can be a convenient adaptable feature.   In their laboratory work the authors have been concerned generally with four grades of carboxylated rubber known as Bisonide 400, P-400, 1600, and 1630 (approximate data are shown in Table VII).

The Bisonide 400 is a general all-purpose polymer, possessing high green strength, made from whole-tire vulcanized rubber.   The P-400 is made from vulcanized truck and bus peels.   It breaks down more readily on the mill and has a lower plasticity and more tack; the vulcanizate has a higher tensile strength and elongation.   Sulfur is normally required for vulcanizing both grades, although sulfur requirements are reduced.

Bisonide 1600 is a tough, nervy, nontacky, but still rubbery material made from whole-tire vulcanized rubber.   It is highly resistant to mechanical breakdown, needs bivalent metallic oxides, diamines, or glycols for vulcanization, and its vulcanizates possess oil resistance and good oven-aging properties.

TABLE VII

PROPERTIES OF CARBOXYLIC RUBBERS

Grade	400	1600	1630
Plasticity (Mooney), ML/212/5-1	40-75	75-125	30-45
Specific gravity	1.15	1.20	1.17
Rubber hydrocarbon, %	48-50	45-50	37-40[a]
Acetone extract, %	20	25	35

[a] Oil-extended types are treated as if rubbery hydrocarbon were 50%.

Bisonide 1630 has the same concentration of active ingredient as the 1600, but is enriched with oil. The reaction and extension with oils are acomplished in a single operation. This material is soft and tacky and more easily worked on the mill, although it still possesses mill nerve and high green strength.

Figure 2 shows that the benzene extract of uncured samples, which have been extracted in acetone for 16 hours, decreases with increased concentration of active ingredient.

COMPOUNDING TECHNIQUES

Processing and compounding techniques vary with the grade of carboxylic rubber polymer used. Although the carboxylated reclaims are generally tough, and the more highly reacted grades lack tack, they respond well to processing. Even after they have been warmed on a mill, they have a rough appearance, which persists in very lightly loaded compounds, but smooth out as the loading is increased. On a cold mill these elastomers soften slightly

TABLE VIII

ZINC OXIDE AS A CURING AGENT

Bisonide 1600		200.0	200.0	200.0	200.0
Stearic acid		—	1.0	1.0	1.0
Zinc oxide		—	2.5	5.0	7.5
	Min.				
Cure at 307° F					
Tensile, lb./sq. inch	15	530	815	1260	1685
	30	705	935	1280	1650
	45	—	1010	1310	1625
Elongation, %	15	390	300	240	210
	30	395	310	250	230
	45	—	360	265	230
Hardness, Shore A	15	41	55	70	80
	30	43	56	71	80
	45	—	58	71	80

during the early stages of milling. Unlike natural rubber, however, the carboxylic rubbers are not progressively softened by continued milling. Exceptions to this rule are the P grades and 1630 grade, which can easily be broken down on the mill. The Bisonides generate considerable heat on a mill or in a Banbury; hence the use of plasticizers is recommended.

The self-reinforcing nature of these carboxylic rubbers is seen in their very high moduli and cured hardnesses. It has been reported[6] that carboxylic nitrile rubbers do not require reinforcing pigments for high tensile strengths. When the carboxylic rubbers from scrap vulcanized rubber under discussion are blended with polychloroprene (Neoprene), the characteristic high modulus and cured hardness are retained. It therefore appears possible to obtain the desired modulus characteristics in polychloroprene compounds by use of these carboxylic rubber hydrocarbons rather than reinforcing fillers. The carboxylic rubbers utilize the same curing mechanism as the polychloroprene. Polymers of desired levels of modulus may be synthesized by incorporating the carboxyl groups in the molecules of the polymer itself, as above indicated, rather than by reliance on reinforcing fillers[30]. Different modulus levels can also be attained by varying the amount of curing agent.

These carboxylic rubbers are effective stiffening agents for unvulcanized rubbers and contain a large portion of useful rubber hydrocarbon. They prevent excessive softness and low plasticity in stocks being processed and could be effective in reducing product defects such as blistering and collapsing. They provide excellent mill roll release, and with the accompanying stiffness should be beneficial in calendered stocks.

TABLE IX
CURING WITH AMINES AHD DIETHYLENE GLYCOL

	Min.	Curing with amines			Curing with diethylene glycol	
Bisonide 1600		200.0	200.0	200.0	200.0	200.0
MT carbon black		90.0	90.0	—	—	—
Hexamethylenetetramine		—	1.0	—	—	—
Hexamethylenediamine		—	—	10.0	—	—
Diethylene glycol		—	—	—	—	5.2
Cure at 307° F						
Tensile, lb./sq. inch	15	—	—	—	530	1090
	20	1075	1390	—	665	1220
	30	—	—	1450	705	1220
Elongation, %	15	—	—	—	390	330
	20	200	150	—	395	300
	30	—	—	170	370	270
Hardness, Shore A	15	—	—	—	41	56
	20	69	75	—	43	57
	30	—	—	78	44	58

CURING MECHANISM

Uncompounded carboxylic rubber polymer can be vulcanized by heat alone, but the physical properties of the vulcanizates are greatly enhanced by the use of curing agents and compounding ingredients. These rubbers require a curing mechanism distinct from that of other polymers and the mechanism varies according to the maleic anhydride that has reacted. Although the 400 grades normally require some sulfur for vulcanization, the requirements are reduced. Zinc oxide as the sole vulcanizing agent cures the 1600 grade to produce very snappy and tight vulcanizates. Table VIII shows the data obtained by incremental increases of the concentration of zinc oxide. Curing with amines or diethylene glycol is shown in Table IX. Cured hardness is unusually high and elongation is low.

It is conceivable that mono- or diamines could react with the carboxyl groups of the chain to form antioxidant elements which are actually built into the vulcanized network[30].

The use of accelerators appears to be of little benefit and certain organic compounds normally used as rubber accelerators, notably 2-mercaptobenzothiazole, retard vulcanization.

Polychloroprene-carboxylic rubber blends can be cured to form practical compounds. Raw natural or Type S synthetic rubber added to the carboxylic rubber does not enhance the physical properties; these are, in fact, lower than those obtained with either rubber alone.

Bivalent metallic oxides, such as zinc oxide, are recommended vulcanizing agents. Consequently, in mixing, they should be the last ingredients added,

just as the sulfur or accelerator is held until last when a rubber batch is mixed. After the metallic oxide has been added, the batch should be treated with the same care as a rubber batch containing an ultra-accelerator.

Brown and Duke[5] have represented the linkages potentially present in zinc oxide vulcanizates of carboxylic nitrile elastomers as follows:

$$
\begin{array}{cccc}
\underset{|}{C}=O & O=\underset{|}{C} & \underset{|}{C}=O & \underset{|}{C}=O \\
O & O-Zn-O & O & O \\
Zn & & Zn & Zn \\
OH & & & O \\
OH & & & \underset{|}{C}=O \\
\underset{|}{C}=O & & & | \\
|
\end{array}
$$
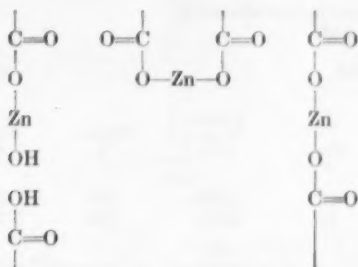
The fact that the carboxylic rubber polymer under consideration can be vulcanized by bivalent metallic oxides, diamines, and glycols suggests that the rubber chains contain carboxyl groups. A procedure has been adapted to the determination of the carboxyl groups on the rubber in question. Vulcanized natural rubber scrap was made to react with an excess of maleic anhydride and the resulting product was hydrolyzed. The product was thoroughly washed and allowed to stand overnight in a known concentration of sodium hydroxide, forming the sodium salt of the acid. Titration with acid to determine the unused portion of sodium hydroxide indicated that 0.84 mole of maleic acid

TABLE X

BISONIDE P-400 COMPOUNDS OF 70 AND 80 SHORE A

Bisonide P-400	200.0	200.0
Antioxidant	2.0	2.0
Diphenylguanidine	0.24	0.24
Benzothiazolyl disulfide	0.8	0.8
Sulfur	3.6	3.6
Stearic acid	2.4	2.4
FT carbon black	20.0	75.0
Zinc oxide	6.0	6.0
Total	235.04	290.04

Cure at 287° F, min.	Tensile, lb./sq. inch	Elong., %	Shore A
15	1705[a]	440	68
30	1770	390	69
45	1750	330	69

	Tensile, lb./sq. inch	Elong., %	Shore A
	1430[b]	330	75
	1575	270	79
	1625	250	80

[a] Temp. of testing, 86.5° F.
[b] Temp. of testing, 88° F.

TABLE XI
BISONIDE 1630 COMPOUND

Bisonide 1630	162.0
Stearic acid	2.0
SRF carbon black	40.0
Sulfur	0.5
Hexamethylenetetramine	1.5
Zinc oxide	5.0
Total	211.0

	Min.	Tensile, lb./sq. inch	Elong., %	Shore A	Modulus 200%
Cure at					
307° F	10	1350	220	78	1325
	15	1375	210	78	1375

added to the vulcanized rubber per mole of iosprene units. It has been concluded that a definite chemical reaction occurs between a mixture of vulcanized natural and Type S synthetic rubbers and unsaturated compounds containing an electrophilic group alpha to the double bond, resulting in an elastomer with carboxyl groups on the polymer chain.

TABLE XII
COMPARISON OF NEOPRENE, WHOLE TIRE RECLAIM, AND BISONIDES IN BLENDS WITH NEOPRENE

Neoprene GN	100.0	70.0	70.0	70.0	70.0	70.0
W. T. reclaim	—	60.0	—	—	—	—
Bisonide P-800	—	—	60.0	—	—	—
Bisonide 800	—	—	—	60.0	—	—
Bisonide 1600	—	—	—	—	60.0	—
Bisonide 1630	—	—	—	—	—	60.0
Magnesia	8.0	6.0	6.0	6.0	6.0	6.0
Antioxidant	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.5	2.5	2.5	2.5	2.5	2.5
Light process oil	15.0	15.0	15.0	15.0	20.0	10.0
MT carbon black	45.0	45.0	30.0	30.0	30.0	30.0
SRF carbon black	80.0	80.0	70.0	70.0	70.0	70.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0
Total	259.5	287.5	262.5	262.5	267.5	257.5
Cure 20 min. at 307° F						
100% modulus, lb./sq. inch	990	710	1110	1125	1120	990
Tensile, lb./sq. inch	1850	1195	1580	1450	1305	1560
Elongation, %	210	200	160	150	120	190
Hardness, Shore A	79	74	83	84	85	80
Heat aged, 70 hr. at 212° F						
Shore A gain, pts.	10	15	9	7	7	8
Tensile gain, %	2	22	17	17	26	10
Elongation loss, %	38	40	25	33	25	32
A.S.T.M. oil 3						
Volume swell, %	67	89	60	55	50	64
Tensile loss, %	29	75	57	53	43	46
Elongation loss, %	5	13	—	0	0	21

TABLE XIII

COMPARISON OF NEOPRENE AND NEOPRENE-BISONIDE BLEND
IN COMPOUND, 60 DUROMETER

Neoprene GN	100.0		66.7
Bisonide 1600	—		66.7
Magnesia	4.0		2.7
Antioxidant	2.0		2.0
MT carbon black	75.0		16.7
Light process oil	10.0		10.0
Stearic acid	0.5		0.5
Petrolatum	1.0		1.0
Zinc oxide	5.0		8.3
2-Mercaptoimidazoline	0.5		0.5
Total	198.0		175.1
Specific gravity	1.42		1.29

	Min.	Tensile, lb./sq. inch	Elong., %	Shore A	Tensile, lb./sq. inch	Elong., %	Shore A
Cure at 307° F	10	1460	650	52	1525	370	61
	15	1460	590	52	1450	320	61

Heat aged, 70 hr. at 212° F (10-min. cure)

Tensile change, %	−1	+17
Elongation loss, %	43	28
Shore A gain, pts.	16	11

TABLE XIV

COMPARISON OF NEOPRENE AND NEOPRENE-BISONIDE BLEND
IN COMPOUND, 80 SHORE A

Neoprene GN-A	100.0		66.7
Bisonide 1600	—		66.7
Magnesia	4.0		2.7
Antioxidant	2.0		2.0
MT carbon black	180.0		120.0
Plasticizer	15.0		15.0
Stearic acid	1.0		1.0
Petrolatum	1.0		1.0
Zinc oxide	5.0		8.3
2-Mercaptoimidazoline	0.5		0.33
Hexamethylenetetramine	—		0.33
Total	308.5		284.06
Specific gravity	1.54		1.43

	Min.	Tensile, lb./sq. inch	Elong., %	Shore A	Tensile, lb./sq. inch	Elong., %	Shore A
Cure at 307° F	10	1105	280	76	1220	180	79
	20	1210	230	79	1240	140	80

		Per cent			Per cent		
Heat aged 70 hr. at 212° F change	10	+12	−70	+18 pts.	+12	−47	+11 pts.
	20	+ 3	−52	+16 pts.	+15	−32	+10 pts.

Oil age, % volume change

ASTM oil 1	− 1	− 0.5
ASTM oil 3	+33.5	+37.5

PROPERTIES OF VULCANIZATES

When cured in the appropriate recipe, these carboxylic rubbers are characterized by good tensiles, high moduli, and high cured hardnesses. The right-hand portion of the graph of Figure 3 shows how the 300 per cent modulus increases with increase in concentration of maleic anhydride above the critical concentration. Table IV illustrates the magnitude of the modulus increase due to the various active ingredients. Table XI shows the increase in modulus that can be expected by blending Neoprene and the carboxylic rubbers. When cured in the test formulation, the increase in cured hardness obtained by the use of

TABLE XV

COMPARISON OF NEOPRENE AND NEOPRENE–BISONIDE BLEND
IN COMPOUND, 80 & 90 SHORE A

Neoprene GN-A	100.0	100.0	70.0	70.0
Bisonide 1600	—	—	—	60.0
Bisonide 1630	—	—	60.0	—
Magnesia	8.0	2.0	6.0	8.0
Antioxidant	4.0	4.0	4.0	4.0
Stearic acid	2.5	1.0	2.5	2.5
Light process oil	15.0	20.0	10.0	15.0
Wood cellulose flock	—	30.0	—	—
MT carbon black	45.0	65.0	30.0	45.0
SRF	80.0	90.0	70.0	80.0
Zinc oxide	5.0	5.0	5.0	5.0
2-Mercaptoimidazoline	—	1.0	—	—
Total	259.5	318.0	257.5	289.5
Specific gravity	1.49	1.50	1.41	1.43
Cure 20 min. at 310° F				
Tensile, lb./sq. inch	1850	1330	1560	1410
Elongation, %	210	110	190	110
Hardness, Shore A	79	92	80	91
Heat aged, 70 hr. at 212° F				
Shore A gain, pts.	10	7	8	5
Tensile gain, %	2	14	10	14
Elongation loss, %	38	73	32	36
ASTM oil 3				
Volume swell, %	67	33	64	49
Tensile loss, %	29	5	46	23
Elongation change, %	−5	+27	−21	−9
Compression set, method B				
22 hr. at 158° F, %	30	22	33	33
Plug aged 22 hr. at 158°				
F, %	25	21	26	27

maleic anhydride, as compared to the corresponding reclaim, is about 20 points Shore A. Use of other unsaturated acids gives increases of 10 to 20 Shore A points.

Table X illustrates a typical formulation for compounding the P-400 grade and the physical properties that can be expected. Shore A hardness is high, with relatively little carbon black or other fillers. These test results were obtained at temperatures of 86° to 88° F. Table XI illustrates the formulation and results obtainable with the 1630 grade. Although the 1630 grade is extended with a large quantity of petroleum oil and contains relatively little additional filler, Shore A hardness and modulus are high. Table XII compares an all-Neoprene compound, a whole tire reclaim-Neoprene blend, and carboxylic

rubber-Neoprene blends in approximately the same formulations. Higher cured hardnesses and moduli are obtained when the carboxylated rubber is used. Tables XIII, XIV, and XV show comparative data obtained with Neoprene compounds and carboxylic rubber-Neoprene blend compounds.

The oven aging of the carboxylic rubbers is good and in blends with Neoprene perhaps slightly improves the aging characteristics of the Neoprene. The Shore A increase on oven aging of the blends is less than that obtained with similar all-Neoprene compounds. The blends generally show higher increases in tensile strength. Although the initial elongations of the blends may be lower than the corresponding all-Neoprene compound, the former retain a greater percentage of their elongation on oven aging[24] (Tables XIII, XIV, and XV).

The volume swell of the blends in ASTM oils 1 and 3 is generally of the same order of magnitude as the all-Neoprene compound (perhaps lower). Consideration of the degree of loading is important. Shore A hardness change of the blends is low and equivalent to the all-Neoprene compound. Tensile strength change in ASTM oil 1 shows the blends have the advantage and the elongation changes of the two are about the same in magnitude. The all-Neoprene compound retains more of its tensile when aged in ASTM oil 3; the elongation change varies[6,21].

Compression set data are shown in Table XV. Some data indicate that zinc oxide acts as a persistent crosslinking agent in the carboxylic rubbers. Conditioning the plug by accelerated aging before testing improves the compression set. Unpublished data show the improvement of set due to conditioning to be far greater for the blends than for the all-Neoprene compounds.

As the concentration of maleic anhydride is increased above the critical point, the torsional hysteresis[22] greatly increases, as shown in Figure 4. Data on results obtained when other active ingredients were used are shown in Table IV. The more highly reacted products show high heat build-up on flexing.

The similarity of curing mechanism and properties of the Bisonides and Neoprene suggested beginning the development program with combinations of the two. Tables XIII, XIV, and XV show the general properties obtainable by blending the low-cost carboxylic rubbers with Neoprene. These compounds should be of sufficient interest to merit further evaluation along practical lines.

ACKNOWLEDGMENT

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APPLICATION OF PAPER CHROMATOGRAPHY TO THE IDENTIFICATION OF ACCELERATORS AND ANTIOXIDANTS *

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DETECTION OF GUANIDINES AND THIOUREAS

Introduction.—The identification of accelerators and antioxidants previously presented many difficulties of a varied character. The accelerators and antioxidants not only occur in relatively small quantities in rubber mixes and in vulcanizates, but many other compounds, originally present in rubber or added during mixing, may interfere with their identification, e.g., by masking the color reactions. In addition, it is possible that the accelerators and the antioxidants cannot be detected in vulcanizates because they are decomposed during mixing, during vulcanization, during aging, and/or during acetone extraction of the rubber.

Bellamy, Lawrie, and Press[1], Parker and Berriman[2], and Mann[3] partially surmounted these difficulties by a chromatographic separation on alumina and on silicagel respectively, prior to identification by means of color reactions or infrared absorption spectroscopy.

Choice of paper chromatography.—The purpose of the present investigations was to investigate the possibilities of the application of paper chromatography to the identification of accelerators and antioxidants. The main advantages of paper chromatography are that it is especially suitable for the separation of small quantities, requires only simple, cheap apparatus, and also that it is applicable to the investigation of closely related compounds. A very important factor is that paper chromatography, more so than other separation methods, not only enables a very nice separation, but also an identification, by a measurement of the R_f-values.

In addition, a separation into groups can be performed by the different methods of isolation and by suitable selection of the mobile phase, of the carrier of the stationary phase, and of the color reactions suitable for the development of the chromatograms. The separations within these groups can be carried out paper-chromatographically.

Paper-chromatographic separation of difficulty soluble compounds.—It is very difficult to separate paper-chromatographically those substances which are insoluble or difficultly soluble in water. To surmount these difficulties it is, however, possible to use some expedients which enable paper-chromatographic separation.

These expedients are based either on modification of the substances to be separated or on modification of the paper.

1. Modification of the substances.

This can be performed by a decomposition into characteristic fragments that dissolve in water or by a synthesis of soluble derivatives, e.g., by coupling the substances with diazotized arylaminesulfonic acids.

2. Modification of the paper.

There are various possibilities.

a. The chromatographic paper is previously buffered at a pH at which the solubility of the substances to be separated will be increased.
b. The chromatographic paper is impregnated with alumina or silica-gel[4]. In this method the partition character is out of the question.
c. It is possible to apply reversed-phase paper chromatography by impregnating the paper with formamide[5], propylene glycol[5], petroleum[6], paraffins[7], latex[8], etc.
d. Complete fibrous acetylation may supply an organophilic carrier of the stationary phase. This question will be discussed later.

Isolation of the compounding ingredients from the rubber mixes and vulcanizates.—During this investigation of the identification of accelerators it appeared that if the accelerator decomposes during vulcanization, a sufficient quantity always remains for detection. In this connection the optimum curing time of the various mixes has not been determined, but the mixes have simply been overcured.

Five g. of the finely divided vulcanized rubber are extracted with acetone for 8 hours in a Soxhlet hot extraction apparatus. In the extract the following substances may occur: free sulfur, softeners, paraffins, stearic acid, amino acids and other compounds of vegetable origin, accelerators, and antioxidants. Because stearic acid, paraffins, and softeners may impede the correct formation of a chromatogram, it is necessary that these substances should be eliminated beforehand, viz., by the preparation of the hydrochloric acid extract, of the ammonia extract or of the alcohol extract. With the preparation of these extracts a separation into various groups is also accomplished.

An outline of the identification of accelerators and antioxidants is given in the following scheme.

SCHEME FOR THE IDENTIFICATION OF ACCELERATORS AND ANTIOXIDANTS

1. Vulcanized rubber ⎧ Paraffins, softeners
          ↓   ⎪ Free sulfur, stearic acid
2. Acetone extract ⎨ Amino acids and other substances
                  of vegetable origin
          ↓   ⎪ Decomposition products
              ⎩ Accelerators and antioxidants

3. a. Hydrochloric acid extract   Guanidine group
                               Amines

    b. Ammonia extract   Mercapto-substituted
                               heterocyclic compounds

         or

    c. Alcohol extract   Antioxidants
      ↓

4. Paper-chromatographic separation and identification.

TABLE I

ACCELERATORS OF THE GUANIDINE GROUP

Structure	Systematic name	Abbreviation	Trade name
	Orthotolylbiguanidine	O.T.B.G.	Vulkacit 1000
	Diphenylguanidine	D.P.G.	Vulkacit D
	Diorthotolylguanidine	D.O.T.G.	D.O.T.G.
	Triphenylguanidine	T.P.G.	T.P.G.

Separation and identification of some derivatives of guanidine.—In the rubber industry four guanidine derivatives are fairly frequently used as vulcanization accelerators. Further particulars about these four compounding ingredients are given in Table I.

These guanidine derivatives can be separated paper-chromatographically. After solution in acetone they are applied upon a 13×56 cm. strip of Whatman paper No. 1, which has previously been buffered at pH = 4. The composition of the buffer solution is 61.45 ml. of 0.1 mol. citric acid and 38.55 ml. of 0.2 mol. secondary sodium phosphate.

The chromatogram is formed by the ascending method, water-saturated butanol-1 being used as the mobile phase. The spots on the chromatograms are made visible by spraying on a 4 per cent solution of sodium hypochlorite. After drying of the chromatogram, the R_f-values are measured.

The color of the reaction products after the reaction with NaOCl, the identification limits both before and after chromatography, and the R_f-values of the four accelerators obtained in the method described are given in Table II.

TABLE II

PROPERTIES OF FOUR GUANIDINE ACCELERATORS

Accelerator	Color of the reaction product	Identification limits		R_f
		Before	After	
		the formation of the chromatogram		
O.T.B.G.	Yellow	20 μg	40 μg	0.35
D.P.G.	Red-brown	5 μg	20 μg	0.64
D.O.T.G.	Red-brown	5 μg	20 μg	0.73
T.P.G.	Yellow-brown	5 μg	20 μg	0.85

The data of Table II clearly confirm the relation between structure and R_f-value of the four substances. The more the guanidine is substituted with groups that decrease the solubility in water, the more its R_f-value increases.

Identification of four guanidine accelerators in rubber mixes and vulcanizates.— Five g. of the finely divided rubber are extracted with acetone for 8 hours in a Soxhlet hot extraction apparatus.

After addition of 10 ml. of 2 N HCl, the dried acetone extract is heated for 15 minutes on a water bath. After cooling, the impurities can be filtered. The filtrate is almost evaporated, neutralized with concentrated ammonia, evaporated again, and finally dissolved in acetone. This solution in acetone containing the guanidine accelerators is applied to the paper by means of a capillary tube or a micropipet. The chromatography is carried out as described above.

Many rubber mixes and vulcanizates have been investigated. It has been found that the accelerators could be identified in all the vulcanizates, with or without fillers, even when only about 0.1 per cent of accelerator was present. There is no interference from pine tar, as in the researches of Bellamy[1]. Only O.T.B.G. may give rise to some difficulties, because the yellow color of its reaction product with sodium hypochlorite is liable to fade during drying of the chromatogram. An example of a chromatogram of the guanidine accelerators is sketched in Figure 1.
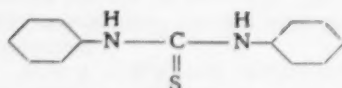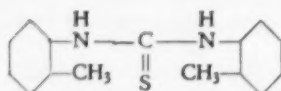
diphenyl thiourea   diorthotolyl thiourea

Identification of diphenyl and diorthotolyl thiourea.—Diphenyl thiourea (thiocarbanilide; Vulkacit C.A.) and diorthotolyl thiourea (A 22) are used as accelerators in the rubber industry.

These thiourea derivatives react readily with ammonia and lead oxide, forming diphenylguanidine and diorthotolylguanidine, respectively. The identification of these compounds has been described above.

$$C_6H_5{-}NH{-}CS{-}NH{-}C_6H_5 \xrightarrow[NH_3]{PbO} C_6H_5{-}NH{-}C({=}NH){-}NH{-}C_6H_5$$
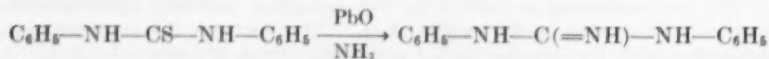
After addition of an excess of PbO the thiourea derivatives are suspended in ammonia in a porcelain crucible. After evaporation and solution in acetone, the excess of PbO and the PbS can be filtered. The filtrate is almost completely evaporated and applied to the paper. The chromatography is carried out exactly as described for the identification of the guanidines.

The identification of the thiourea derivatives in rubber mixes and vulcanizates is accomplished in the following manner:

Five g. of the finely divided rubber are extracted with acetone for eight hours in a Soxhlet hot extraction apparatus. 15 ml. of 4 N ammonia and an excess of lead oxide are added to the nearly evaporated acetone extract. After evaporation, 15 ml. of acetone are added. The impurities are filtered and the filtrate is evaporated. Its hydrochloric acid extract is applied to the chromatographic paper, and the chromatogram is formed as described above.
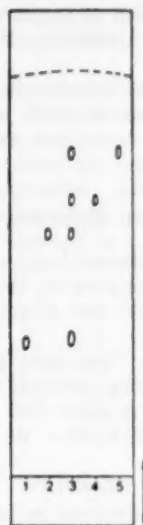
Fig. 1.—Chromatogram of the guanidine accelerators.

1. O.T.B.G.
2. D.P.G.
3. Mixture of 1, 2, 4, and 5
4. D.O.T.G.
5. T.P.G.

TABLE III

FOUR COMPOUNDING INGREDIENTS OF THE "MERCAPTO GROUP"

Systematic name	Structure	Function	Trade name
2—mercaptoimidazoline		Accelerator	N.A.22
2—mercaptothiazoline		Accelerator	2—M.T.
2—mercaptobenzimidazole		Antioxidant	M.B.
2—mercaptobenzothiazole		Accelerator	Captax Vulkacit Merkapto

It is possible to get some idea of the accelerator consumption from the dimension of the spots and the intensity of the colors of the spots on the chromatograms.

From the analysis of some vulcanizates accelerated with diphenyl or diorthotolyl thiourea the conclusion could be drawn that the accelerators originally present in the mixes decompose gradually during the cure and are completely consumed in the end.

DETECTION OF SOME HETEROCYCLIC COMPOUNDS

A number of mercapto-substituted heterocyclic compounds are frequently used as accelerators and antioxidants in the natural and synthetic rubber industry.   More particulars about four of these compounding ingredients are given in Table III.

The four compounds of the "mercapto group" are separated by paper chromatography by the descending method, using water-saturated butanol-1 as the mobile phase and Whatman paper No. 1 as the carrier of the stationary phase, either directly or buffered at pH = 10.

TABLE IV

PROPERTIES OF THE COMPOUNDS OF THE "MERCAPTO GROUP"

| | Identification limits | | R_f—values | |
| | Before formation of the chromatogram (μg) | After the chromatogram (μg) | | |
Name			Unbuffered	Buffered at pH = 10
2—mercaptoimidazoline	5	20	0.56	0.54
2—mercaptothiazoline	1	10	0.76	0.78
2—mercaptobenzimidazole	1	2	0.85	0.86
2—mercaptobenzothiazole	5	10	0.91	0.54

The spots can be made visible by spraying a 5 per cent solution of bismuth nitrate in 0.5 N nitric acid on the dried chromatogram.   When only small quantities of these compounding ingredients are present, the spots are not visible in daylight, but they are in ultraviolet light.

The identification limits before and after chromatographic separation and the R_f-values, both for buffered and for unbuffered strips, are given in Table IV. Examples of the two chromatograms are sketched in Figure 2.   Table IV and Figure 2 give rise to the following remarks:

The difference in structure between 2-mercaptoimidazoline and 2-mercapto-thiazoline is approximately equal to the difference in structure between a secondary amine (—NH—) and a thioether (—S—).   It is not surprising therefore that the R_f-value of the first compound is less than the R_f-value of the second, because secondary amines generally dissolve better in water than do the analogous thioethers.   Consequently in an equilibrium partition between water and an organic solvent the water phase is favored by the imidazoline rather than by the thiazoline derivatives.   The same argument holds for 2-mercpatobenzimidazole and 2-mercaptobenzothiazole.

It is also easily understood that the R_f-values of 2-mercaptoimidazoline and 2-mercaptothiazoline are lower than those of 2-mercaptobenzimidazole and 2-mercaptobenzothiazole.

The difference between the R_f-values of 2-mercaptobenzimidazole and 2-mercaptobenzothiazole is so small as to make it possible that in mixes of unknown

composition no unambiguous conclusion can be drawn. It is therefore preferable to form chromatograms on buffered papers, too, in which case the R_f-values differ more.

Identification of the compounding ingredients of the "mercapto-group" in rubber mixes and vulcanizates.—A detailed description of the identification procedure in rubber is given below.

Five g. of the finely divided rubber are extracted with acetone for eight hours in a Soxhlet hot extraction apparatus. The acetone extract is evaporated and heated for 15 minutes on a water bath, after addition of 20 ml. of 4 N ammonia. The ammonia extract always has a yellow or brown color, and is
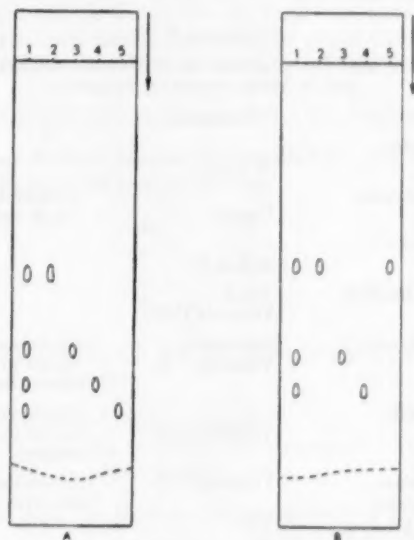
FIG. 2.—Chromatogram of the mercapto group.

A. Unbuffered papers
B. Strips, buffered at pH = 10

1. Mixture of 2, 3, 4, and 5
2. N.A.22
3. 2-MT
4. M.B.
5. Captax

fairly turbid. The filtration takes a long time. For this reason 2 ml. of a 5 per cent solution of strontium chloride are added to the cooled ammonia extract[9]. The strontium salts of the fatty and other acids are precipitated, together with colloidal substances. The filtration can now be carried out easily. The filtrate is evaporated, neutralized with dilute hydrochloric acid, evaporated again, and dissolved in acetone. The acetone solution is now applied to the paper. The chromatographic procedure has been given above.

In all the mixes and vulcanizates investigated the mercapto compound could be identified readily. In addition it has been found that in the ammonia extracts, after evaporation and after addition of some drops of water, the characteristic odor of 2-mercaptobenzothiazole could be observed when the rubber

to be investigated contained this accelerator. This very simple method is even more sensitive than the chromatographic one.

Salts and derivatives of 2-mercaptobenzimidazole and 2-mercaptobenzothiazole.—There are various salts and derivatives of 2-mercaptobenzimidazole and 2-mercaptobenzothiazole which are used in the rubber industry.

These compounding ingredients are collected in Table V.

During isolation of the compounding ingredients of the mercapto group from the rubber and during elimination of paraffins, stearic acid, etc., the accelerators and antioxidants undergo various pretreatments in succession, as described above. These pretreatments may affect the molecular composition of the compounding ingredients considerably. Thus M.T.B.Z. ($R_f = 1.0$) is

TABLE V

SOME SALTS AND DERIVATIVES OF 2-MERCAPTOBENZIMIDAZOLE
AND 2-MERCAPTOBENZOTHIAZOLE

Systematic name	Trade name	Particulars
Zinc salt of 2-mercapto-benzimidazole	M.T.B.Z.	
Copper salt of 2-mercapto-benzothiazole	Cuprax	Relatively large amounts of Cu in the ash of the rubber
Zinc salt of 2-mercapto-benzothiazole	O.X.A.F.	
Di-2-benzothiazolyl disulfide	Altax Vulkacit DM	
N-cyclohexyl-benzothiazolyl-2-sulfenamide	Santocure Vulkacit C.Z.	Cyclohexylamine can be detected in the hydrochloric acid extract
N-diethyl-benzothiazyl-2-sulfenamide	Vulkacit A.Z.	Diethylamine can be detected in the hydrochloric acid extract
N-pentamethylene-benzo-thiazolyl-2-sulfenamide	Vulkacit B.Z.	Piperidine can be detected in the hydrochloric acid extract
8,8'-di-2-benzothiazolyl-N,N'-dimethylthiol urea	El-sixty	
2,4-dinitrophenyl thiobenzo-thiazole	e.g. in Ureka and in Ureka Blend B	Only in one vulcanizate could Captax be detected
Benzothiazolyl-thiobenzoate	Ureka C	

completely converted into 2-mercaptobenzimidazole ($R_f = 0.85$). Further it appeared that the copper and the zinc salts of 2-mercaptobenzothiazole are partly or completely converted into the free thiol under the influence of the preceding treatments.

In the same manner di-2-benzothiazolyl disulfide has been found to be decomposed to 2-mercaptobenzothiazole by the preceding treatment. It is therefore impossible to determine by the newly developed method whether Altax or Captax is present in a rubber mix or in a vulcanizate.

The various pretreatments do not decompose the accelerator Santocure (N-cyclohexyl 2-benzothiazolylsulfenamide), but the acetone extraction does. However, this decomposition gives rise not only to 2-mercaptobenzothiazole (which will occur in the ammonia extract), but also to cyclohexylamine (which will occur in the hydrochloric acid extract).

The detection of this cyclohexylamine will be described in the next section.

Diethylamine and piperidine may be correspondingly identified in the hydrochloric acid extracts of the acetone extracts of rubber accelerated with Vulkacit AZ and Vulkacit BZ, respectively.

In the ammonia extracts of such vulcanizates the 2-mercaptobenzothiazole may be detected. In vulcanizates accelerated with Ureka C or El-sixty the identity of 2-mercaptobenzothiazole is easily confirmed. However, in Ureka and in Ureka Blend B the 2,4-dinitrophenyl thiobenzothiazole does not decompose either through the influence of the necessary pretreatments or due to the hot acetone extraction.

A number of rubber mixes and vulcanizates containing accelerators or antioxidants, mentioned in Table III or Table IV have been investigated. Their identities have been readily confirmed by paper chromatography, except in the case of vulcanizates accelerated with 2,4-dinitrophenyl thiobenzothiazole.

DETECTION OF DITHIOCARBAMATES AND THIURAM SULFIDES

Detection of some dithiocarbamates.—A number of ultra accelerators, used in the rubber industry, have the general formula

$$R_1 \diagdown \atop R_2 \diagup N - C(=S) - SM$$
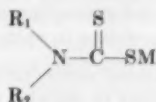
M is a metal (Zn, Cd, Bi, Cu, Pb, Na, Se or Te) or a secondary amine. R_1 and R_2 may be various groups:

$R_1 = R_2$ is methyl, ethyl, butyl, or benzyl.
$R_1 = $ ethyl $\qquad R_2 = $ phenyl or cyclohexyl
$R \;\; = $ methyl $\qquad R_2 = $ phenyl

R_1 and R_2 form with the N-atom the ring system of piperidine.

Generally these salts of the dithiocarbamic acids are difficultly soluble in water. However, it is possible to decompose these dithiocarbamates into secondary amines by means of dilute hydrochloric acid. These amines are better soluble in water, so that they can be separated paper-chromatographically.

The hydrochlorides of the amines, dissolved in water, are placed on Whatman paper No. 1 by means of a micropipet or a capillary tube. The chromatogram is formed by the ascending method, using butanol-1, saturated with 0.5 N HCl, as the mobile solvent. This hydrochloric acid has two functions. In the first place it is used to maintain an acid medium, because in alkaline medium the amines are volatile. In the second place the hydrochloric acid decreases the ionization of the hydrochlorides of these amines. In consequence the tailing of the spots is reduced. Too much strong acid, however, should be avoided in view of a possible effect on the filter paper.

Two color reactions are suitable for the development of the chromatograms:

1. Spraying the paper with a mixture of ethanol, carbon disulfide, and triethylamine, the secondary amines can be resynthesized to dithiocarbamates[10]. These dithiocarbamates can be detected by spraying a copper solution, as a

<div align="center">

TABLE VI

IDENTIFICATION LIMITS AND R_f-VALUES OF VARIOUS AMINES

</div>

| Amines | Identification limits (in μg) | | | | R_f-value |
| | Before separation | | After separation | | |
	Reagent a	Reagent b	Reagent a	Reagent b	
Dimethylamine	2	<1	10	1	0.12
Diethylamine	2	1	10	10	0.31
Dibutylamine	2	1	10	5	0.70
Piperidine	2	<1	20	2	0.29
Dibenzylamine	—	1	—	10	0.79
Ethylcyclohexylamine	—	—	—	±50	0.56
Cyclohexylamine	—	—	—	±50	0.51

result of which brown colors are formed on the spots where the amines were originally present.

A disadvantage of this method is that diethylamine and piperidine, having almost equal R_f-values, cannot be distinguished by this color reaction.

2. Ninhydrin and secondary aliphatic amines give blue reaction products of unknown composition. In the presence of cadmium ions, the reaction colors are pink and the reaction is more sensitive. Piperidine, however, gives a violet color. By means of this color reaction with ninhydrin it is possible to distinguish diethylamine and piperidine in spite of the equal R_f-values.

Ninhydrin also reacts with amino acids, primary amines, etc. The identification of dithiocarbamates present in natural rubber vulcanizates may therefore be interfered by the coloring of the amino acids.

FIG. 3.—Chromatogram of four amines.

1. Piperidine
2. Mixture of 3, 4, and 5
3. Dibutylamine
4. Diethylamine
5. Dimethylamine

FIG. 4.—Chromatogram of four amines.

1. Dibenzylamine
2. Diethylamine
3. Cyclohexylamine
4. Piperidine.

These difficulties are eliminated when, for the detection of the dithiocarbamates in vulcanizates of unknown composition, two chromatograms are formed, one of these being developed with ninhydrin, the other with $CuSO_4$ after synthesis of the dithiocarbamates.

The composition of the color reagents is:

1. A mixture of 50 ml. of ethanol, 50 ml. of carbon disulfide, and 2 ml. of triethylamine; after drying, a 2 per cent solution of copper sulfate.

2. A 0.2 per cent solution of ninhydrin in 96 per cent ethanol, containing 2 per cent of acetic acid and 0.5 per cent of cadmium acetate.

The identification limits and the R_f-values of various amines are given in Table VI. Examples of the chromatograms are sketched in Figures 3 and 4.

For the detection of the various dithiocarbamates in rubber mixes and vulcanizates, with or without fillers, the following method is used.

Five g. of finely divided rubber are extracted with acetone for eight hours in a Soxhlet hot extraction apparatus. The dried acetone extract is heated on a water bath with 10 ml. of 2 N hydrochloric acid. After cooling, the undissolved impurities are removed by filtration and washed with 5 ml. of 2 N HCl. The filtrate and the washing liquid are combined and evaporated, whereupon the residue is dissolved in some drops of water and applied to the paper.

The chromatographic separation is carried out exactly as described above. For each vulcanizate two chromatograms are formed.

A number of vulcanizates of varying composition, both with and without fillers, have been investigated. In all these rubber compounds the amines, formed by the acid decomposition of the dithiocarbamates, have been separated and identified.

Detection of zinc methylphenyl dithiocarbamate and zinc ethylphenyl dithiocarbamate.—Zinc ethylphenyl dithiocarbamate (Vulkacit P extra N) is frequently used as an accelerator in the rubber industry. Zinc methylphenyl dithiocarbamate is formed from dimethyldiphenyl thiuram disulfide (Vulkacit J) during vulcanization or acetone extraction.

N-ethylaniline and N-methylaniline respectively are formed from these dithiocarbamates by decomposition with dilute acids. The detection of these amines, however, has presented many difficulties, particularly because no suitable color reagent could be found. The common reactions for substituted anilines cannot be applied, because of their aggressive nature and their lack of sensitivity. General sprays for the detection of spots on chromatograms have also failed.

However, it is possible to color these amines before chromatography by coupling them with diazotized sulfanilic acid and subsequently to separate the azodyes formed.

For the detection of these dithiocarbamates in rubber mixtures and in vulcanizates the following method may be used.

Five g. of the finely divided rubber are extracted with acetone for eight hours in a Soxhlet hot extraction apparatus. The dried acetone extract is heated with 15 ml. of 2 N HCl on a water bath. Impurities and undissolved substances are removed by filtration. The filtrate, containing methyl- and ethylaniline, is evaporated and applied to the paper (Whatman No. 1). The amines on the paper are coupled with diazotized sulfanilic acid[11], neutralized with a drop of 2 N ammonia, and dried. The best mobile phase is butanol saturated with 2 N ammonia. The spots on the chromatograms, however, are

somewhat tailed.   However, the front of the spot of 3-ethylamino-3'-sulfo-
azobenzene has travelled a slightly greater distance than the front of the spot of
3-methylamino-3'-sulfoazobenzene (see Figure 5).

In view of this tailing of the spots it is better to form at the same time a
chromatogram of the dyes of these anilines as such.   Methylaniline and ethyl-
aniline have been detected in all the vulcanizates containing a methylphenyl
or an ethylphenyl dithiocarbamate, except in the vulcanizates containing both
accelerators, in which case the spots of the two amines partially overlapped.

Simultaneous detection of thiuram sulfides and dithiocarbamates.—In the
rubber industry various thiuram sulfides of the general formula: $R_1R_2N.CS$—
$(S)_x$—$CS.N.R_1R_2$ are used not only as accelerators, but in case $x \geqslant 2$ also as
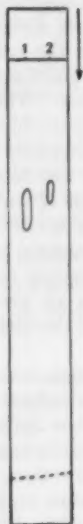
Fig. 5.—Chromatogram of secondary amines,
coupled with diazotised sulfanilic acid.

1. Ethylaniline
2. Methylaniline

vulcanizing agents.   A number of investigators have found that these thiuram
sulfides decompose to the analogous dithiocarbamates during vulcanization.
This decomposition may also occur under the influence of the acetone extrac-
tion.   For the identification of the dithiocarbamates we have made use of their
decomposition in acid medium into secondary amines.   However, some
thiuram sulfides also give rise to the same decomposition products by reaction
with hydrochloric acid.   It is therefore very difficult to decide whether a
thiuram sulfide or a corresponding dithiocarbamate is present in a rubber
vulcanizate.

However, Hilton and Newell[12] have developed a method for the simultane-
ous quantitative determination of thiuram sulfides and dithiocarbamates of
known composition.   The principles of their method have been applied to the
simultaneous detection of these compounds in rubber mixes and in vulcanizates.

Two g. of the finely divided rubber are extracted with acetone for eight

hours in a Soxhlet hot extraction apparatus. The acetone extract is made up to about 10 ml. Some drops of a 2 per cent copper sulfate solution are added to 5 ml. of this extract. A dark brown color immediately appears when a dithiocarbamate is present. From the other 5 ml. of extract the carbon disulfide is eliminated by boiling after addition of a small excess of phosphoric acid. When the carbon disulfide has been completely eliminated—which can be verified in a separate test with a few drops of $CuSO_4$—the solution is neutralized with 20 per cent sodium hydroxide and reduced with sodium bisulfite. The acetone is evaporated. The residue is divided into two equal parts. To the first part are added concentrated ammonia, ammonium citrate, and chloroform; to the second part are added equal quantities of ammonia, ammonium citrate, and chloroform, together with some drops of a 2 per cent $CuSO_4$ solution. After shaking, the chloroform layer of the second part will be colored dark brown if a copper dithiocarbamate is formed, which means that originally a thiuram sulfide was present. Because the acetone extract of vulcanizates often have a brown color, it is desirable to make a comparison experiment without copper sulfate.

It has been found that this method is very satisfactory if it has to be decided whether a thiuram sulfide or a dithiocarbamate is present in a vulcanizate. The determination of the groups R_1 and R_2 can be carried out according to the method described for the detection of ultra-accelerators of the dithiocarbamate type. However, up till now it has been impossible to determine whether the thiuram sulfide present in a rubber mix or a vulcanizate is a mono-, di- or tetrasulfide.

A number of rubber mixes and vulcanizates, containing various thiuram sulfides have been investigated. It has been found that not only thiuram sulfides, but also dithiocarbamates could be detected in the acetone extracts of these rubbers. The conclusion may thus be drawn that thiuram sulfides partly decompose during acetone extraction of the rubber.

DETECTION OF ANTIOXIDANTS

Identification of antioxidants with a primary or a secondary amino group.— These antioxidants are insoluble or difficultly soluble in water, and for this reason they cannot be separated chromatographically on untreated papers. We have stated previously what expedients can be used for the paper-chromatographic separation of difficultly soluble compounds. Two of these expedients promised results for the problem of the identification of antioxidants. In the first place we tried to couple these antioxidants with diazotized arylaminosulfonic acids[13]. In this way a very interesting chromatogram was formed of phenyl-2-naphthylamine (P.B.N.), coupled with various diazotized amines. The R_f-values of the coupled products on a chromatogram (descending method) are given in Table VII. Water-saturated phenol was used as the mobile phase (Figure 6).

From Table VII and Figure 6 it appears that the R_f-values of the dyes decrease when more sulfonic groups are present in the molecule, and consequently in the equilibrium partition of the dyes between water and phenol the water phase is more favored.

The coupled products of phenyl-1-naphthylamine (P.A.N.) have the same R_f-values as the corresponding P.B.N. derivatives. Although P.A.N. and P.B.N. cannot be separated in this way, it is still possible to distinguish them,

TABLE VII

R_f-VALUES OF COUPLED PRODUCTS OF P.B.N. WITH VARIOUS
DIAZOTIZED ARYLAMINOSULFONIC ACIDS

P.B.N. with diazotized sulfanilic acid	R_f 0.77
P.B.N. with diazotized 1-naphthylamino-3,6-disulfonic acid	R_f 0.29
P.B.N. with diazotized 2-naphthylamino-3,6-disulfonic acid	R_f 0.35
P.B.N. with diazotized 2-naphthylamino-6,8-disulfonic acid	R_f 0.35
P.B.N. with diazotized 1-naphthylamino-3,5,7-trisulfonic acid	R_f 0.18

because the dyes derived from P.A.N. are blue in acid medium, whereas the analogous P.B.N. derivatives are red. In alkaline medium they are all red.

In the second place we attempted to apply another method, viz., modification of the filter paper by acetylation[14].

Separation and identification of antioxidants with an amino group.—It has been found that completely acetylated Whatman paper No. 1 can be used with excellent results as the carrier of the stationary phase for the chromatographic separation of antioxidants. A mixture of equal volumes of benzene and 96 per cent ethyl alcohol is a good mobile phase. A suitable color reagent is a 4 per cent solution of benzoyl peroxide in benzene, because of its organic solvent (the acetylated paper is not wetted by aqueous solutions) and because this reagent gives different colors with the vairous antioxidants.

The antioxidants investigated, the colors obtained by the reaction with benzoyl peroxide, the identification limits of this reaction both before and after the separation, and the R_f-values measured on acetylated paper with benzene-ethanol (1:1) as the mobile phase are mentioned in Table VIII. Some chromatograms are given in Figures 7 and 8.

Identification of antioxidants with an amino group in rubber.—Because of the insolubility in dilute hydrochloric acid and in dilute ammonia, the antioxi-
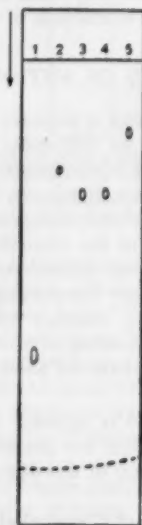
FIG. 6.—Chromatogram of P.B.N., coupled
with various diazotized arylaminosulfonic
acids (see Table VII).

TABLE VIII

PAPER-CHROMATOGRAPHIC DETECTION OF ANTIOXIDANTS

Systematic name	Trade name	Color reaction product	Identification limits in 10^{-6} g.		R_f-values
			Before chromatogr. separation	After chromatogr. separation	
Phenyl-1-naphthylamine	Neozone A Nonox A Alterungsschutzmittel P.A.N.	Light yellow	5	10	0.64
Phenyl-2-naphthylamine	Neozone D Nonox D Alterungsschutzmittel P.B.N.	Blue-grey	5	20	0.64
Diphenyl-p-phenylenediamine	J.Z.F.	Yellow-orange	<1	2	0.56
Phenyl-cyclohexyl-p-phenylenediamine	Alterungsschutzmittel 4010	Yellow	<1	10	0.73
Di-2-naphthyl-p-phenylene-diamine	Agerite White Santowhite C.I. Nonox C.I. Alterungsschutzmittel D.N.P. Antioxidant 123	Pink	1	5	0.55 (Tailing)
p-Isopropoxydiphenylamine	E.g. in Agerite Hipar, a mixture of 2, 3, and 6	Yellow-brown	—	—	0.73
p,p'-Dimethoxydiphenylamine	E.g. in Thermoflex A, a mixture of 2, 3, and 7	Brown-pink	—	—	0.68
p-(p-Tolylsulfonylamino)-diphenylamine	Aranox	Brown-red	<1	5	0.65
p-(p-Tolylsulfonylamino)-phenyl-p-tolylamine	M.U.F.	Red	1	5	0.65
Mono- and diheptyldiphenyl-amine	Agerite Stalite	Green	—	—	0.81 0.91
2,4-Diaminodiphenylamine	Oxynone	Brown	<1	10	0.38
p,p'-Diaminodiphenylmethane	Tonox	Red-brown	2	40	0.50
Diphenylethylenediamine	Stabilite	Red-brown	10	80	0.65
Di-o-tolylethylenediamine	Stabilite Alba	Red-brown	10	80	0.67

dants cannot be isolated from the acetone extract by the preparation of an acid or an alkaline extract.

However, the preparation of an alcohol extract is safisfactory in most cases for this purpose. For the detection of antioxidants with an amino group in rubber the following method has been applied.

Five g. of the finely divided rubber mix or vulcanizate are extracted with acetone for eight hours in a Soxhlet hot extraction apparatus. The acetone extract is evaporated, dissolved in 5 ml. of 96 per cent ethanol, and boiled. After cooling, the impurities are filtered. The filtrate is evaporated to a small volume and applied to acetylated Whatman paper No. 1. The chromatogram is formed as described above.
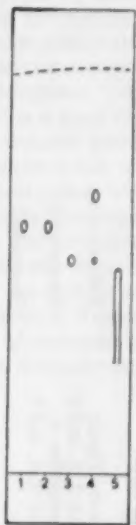
FIG. 7.—Chromatogram of antioxidants.

1. P.A.N.
2. P.B.N.
3. J.Z.F.
4. 4010
5. Agerite White

FIG. 8.—Chromatogram of antioxidants.

6. Aranox
7. M.U.F.
8. Agerite Stalite
9. Thermoflex A
10. Agerite Hipar

A number of vulcanizates containing various antioxidants with an amino group have been investigated. It has been found that Oxynone could not be identified in vulcanizates. Tonox could not be detected in vulcanizates containing 40 per cent of carbon black, but in pure gum mixes it could. The presence of Stabilite and Stabilite Alba could be easily determined, but it is not possible to distinguish between these antioxidants.

The other antioxidants did not present any difficulties.

Detection of phenolic antioxidants.—In the literature various methods for the paper-chromatographic separation of phenols have been described. None of these methods, however, is suitable for the separation and identification of the phenolic antioxidants. It was therefore tried to apply the acetylated paper for this problem, too.

TABLE IX

CHROMATOGRAPHIC DETECTION OF ANTIOXIDANTS

Systematic name	Trade name	Identification limits in 10^3 g.		R_f-values	
		Before chromatogr. separation	After separation	Mobile phase 1	Mobile phase 2
2,6-Di-tert-butyl-4-methylphenol	Ionol Deenax	10	80	0.60	0.44
2,2'-Methylene-bis (4-methyl-6-tert-butylphenol)	2246	1	10	0.66	0.55
2,5-Di-tert-amyl-hydroquinone	Santovar A	1	40	0.69	0.53 T
2,5-Di-tert-butyl-hydroquinone	Santovar O	1	10	0.71	0.55 T
Hydroquinone-monobenzylether	Agerite Alba	10	10	0.66	0.28 T
4,4'-Dihydroxybiphenyl	Alterungs-schutzmittel D.O.D.	1	2	0.77	0.43 T
4,4'-Thio-bis (6-tert-butyl-3-methylphenol)	Santowhite Crystals	10	40	0.71	0.63 T
4,4'-Thio-bis (2,5-d-tert-amyl-phenol)	Santowhite L	10	40	0.68	0.70 T
4,4'-Butylidene-bis (6-tert-butyl-3-methylphenol)	Santowhite Powder	10	40	0.69	0.73 T

T means: tailing of the spot.

Although a commercially available acetylated paper (Schleicher and Schüll 2043 b azetyliert) gives sufficient separations, it is not used in our laboratory because of the irreproducible R_f-values obtained with it.

This lack of reproducibility is caused by its heterogeneity.   The saponification number of this commercial paper varies not only for different sheets, but also in one paper as much as 200–300 mg. of KOH per gram.
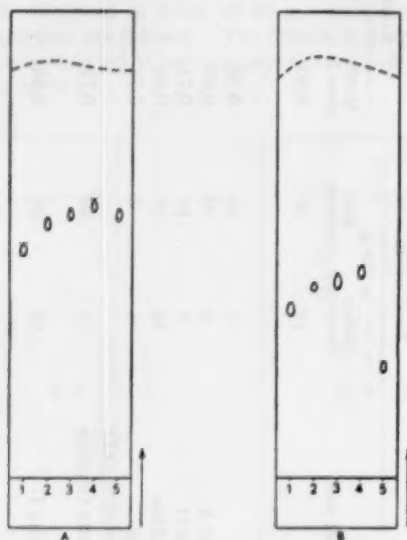
FIG. 9.—Chromatogram of phenolic antioxidants.

1. Ionol
2. 2246
3. Santovar A
4. Santovar O
5. Agerite Alba

A. Butyl acetate-pyridine-methanol-water (1:5:1:3)
B. Propanol-2-methanol-water (3:3:2).

The investigation was therefore continued with the homemade, completely acetylated paper.   The following mobile phases were used.

1. Butyl acetate-pyridine-methanol-water   1:5:1:3.
2. Propanol-2-methanol-water   3:3:2.

The following color reagents have been applied for the detection of the phenols on the chromatograms:

a. Tollens' reagent.   Two drops of 2 N NaOH are added to 0.5 ml. of 5 per cent AgNO$_3$.   The precipitate is dissolved in the smallest possible amount of 2 per cent ammonia.   The reagent is diluted with an equal quantity of 96 per cent ethanol.
b. Millon's reagent.   One part by weight of mercury is dissolved in one part of fuming nitric acid, and subsequently diluted with two parts of water and two parts of 96 per cent ethanol.

Tollens' reagent blackens the spots of all phenolic antioxidants and Millon's reagent generally gives yellow colors. Only Agerite Alba gives with Millon's reagent a characteristic lemon-yellow color.

Table IX lists the phenolic antioxidants investigated, their trade names, the identification limits for the reaction with Tollens' reagent before and after the chromatographic separation with mobile phase 1, and the R_f-values obtained with both mobile phases.

Some chromatograms are given in Figure 9.

By the application of two color reagents and two mobile phases it is in many cases possible to identify the phenolic antioxidants mentioned in Table IX.

Identification of phenolic antioxidants in rubber.—The presence of antioxidants with an amino group does not disturb the detection of the phenolic antioxidants when a mixture of methanol-propanol-2-water (3:3:2) is used as the mobile phase. The correct formation of the chromatogram on the other hand is impeded by the presence of stearic acid and paraffins. In some cases these disturbing substances can be eliminated by the preparation of an ethanol extract and by the addition of strontium chloride.

The following method has been applied for the identification of phenolic antioxidants in rubber mixes and in vulcanizates.

Five g. of the finely divided rubber are extracted with acetone for eight hours in a Soxhlet hot extraction apparatus. The acetone extract is evaporated and dissolved in about 5 ml. of 96 per cent ethanol. After addition of 3 drops of 20 per cent $SrCl_2$ and 3 drops of 4 N ammonia, the impurities are filtered. The filtrate is evaporated to a small volume and placed on a strip of acetylated Whatman paper No. 1. Two chromatograms are formed by the ascending method, with two mobile phases, and developed with the two color reagents mentioned above.

It has been found that only in vulcanizates containing Agerite Alba or Alterungsschutzmittel D.O.D. could an unambiguous identification be performed. The chromatograms of the extracts of other vulcanizates showed more than one spot, probably caused by various oxidation products of the antioxidants. Because these other spots could be observed in the investigation of uncured rubber mixes, too, the conclusion may be drawn that this undesirable oxidation takes place during acetone extraction and under the influence of the various pretreatments.

It appeared that no better results could be obtained by employing other extracting solvents or when reducing substances were added to the extraction flask.

DETECTION OF ACCELERATORS AND ANTIOXIDANTS IN RUBBER OF UNKNOWN COMPOSITION

In most cases a quantity of 17 grams of a rubber mix or of a vulcanizate has been found to be sufficient for the application of the identification method.

Although the detection of the compounding ingredients in rubber of unknown composition can be performed with considerably smaller quantities of rubber, it is recommended not to investigate smaller amounts, if possible, because it is not known in what concentration the accelerators and antioxidants occur in the rubber and because these compounds may be decomposed or modified during vulcanization, during aging, during acetone extraction, etc.

The identification method is given in the outline below.

ISOLATION AND SEPARATION INTO VARIOUS GROUPS

I. Five g. of the finely divided rubber are extracted with acetone for eight hours in a Soxhlet hot extraction apparatus. The dried acetone extract is boiled for 15 minutes with 10 ml. of 2 N HCl. After cooling, the impurities are filtered and washed with 5 ml. of 2 N HCl. The filtrate and the washing liquid Ia and the residue Ib are investigated separately.

Scheme of the Identification Method

17 g rubber mix or vulcanisate

I. 5g acetone extract	II. 5g acetone extract	III. 5g acetone extract	IV. 2g acetone extract

Ia HCl extract | Ib residue | IIa NH_4OH extract | IIb residue | IIIa C_2H_5OH extract | residue

Heating with PbO and NH_4OH

Iba HCl extract | residue

→ A. guanidines

→ B. amines

→ C. amines

→ D. amines

→ E. mercaptogroup

→ F. mercaptogroup

K dithiocarbamates and thiuram sulphides

→ G. antioxidants with amino group

→ H. phenolic antioxidants

→ I phenolic antioxidants

* If an insufficient quantity of rubber is available, the antioxidants can be found in the residue IIb. It is then necessary to prepare the alcohol extract III of the residue IIb.

The filtrate and the washing liquid Ia are combined and evaporated. One part is dissolved in water: B, C, and D. The remainder is neutralized with concentrated ammonia, evaporated again, and dissolved in acetone: A.

The residue Ib is dissolved in acetone, placed in a porcelain crucible, evaporated, and heated after addition of 15 ml. of 4 N ammonia and of a small excess of PbO. After evaporation the residue is dissolved in acetone and the impurities are filtered.

The filtrate is evaporated, and boiled for 15 minutes in 10 ml. of 2 N HCl. After cooling, the impurities are filtered and washed with 5 ml. of 2 N HCl.

The filtrate and the washing liquid are combined, evaporated, neutralized with concentrated ammonia, evaporated again, and dissolved in acetone: A.

II. Five g. of the finely divided rubber are extracted with acetone for eight hours in a Soxhlet hot extraction apparatus. The dried acetone extract is dissolved in 20 ml. of 4 N ammonia and boiled. After cooling, 2 ml. of 5 per cent $SrCl_2$ are added. After stirring, the impurities are filtered and washed with 10 ml. of 4 N ammonia. The filtrate and the washing liquid are combined, evaporated, neutralized with dilute hydrochloric acid, evaporated again, and dissolved in acetone: E and F.

III. Five g. of the finely divided rubber are extracted with acetone for eight hours in a Soxhlet hot extraction apparatus. The dried acetone extract is dissolved in 5 ml. of 96 per cent ethanol. After addition of 3 drops of 20 per cent $SrCl_2$ and 3 drops of 4 N ammonia, the impurities are filtered. The filtrate is evaporated to a small volume: G, H, and I.

IV. Two g. of the finely divided rubber are extracted with acetone for eight hours in a Soxhlet hot extraction apparatus: K. The acetone extract is made up to 10 ml. Some drops of 2 per cent $CuSO_4$ are added to 5 ml. of this extract. A dark brown color immediately appears when a dithiocarbamate is present. In the other 5 ml. of the extract the dithiocarbamate is decomposed by boiling, after addition of a small excess of phosphoric acid. When all the carbon disulfide has been removed—which may be checked in a separate test by means of some drops of 2 per cent $CuSO_4$—the solution is neutralized with 20 per cent NaOH and reduced with sodium bisulfite. The acetone is removed by boiling. After cooling, the remainder is divided into two equal parts. To the first part are added concentrated ammonia, ammonium citrate, and chloroform; to the second part, equal volumes of ammonia, ammonium citrate, and chloroform, and in addition some drops of 2 per cent $CuSO_4$ are added. When, after shaking, the chloroform layer of the second part is colored dark brown, this proves that a copper dithiocarbamate is formed and consequently that originally a thiuram sulfide was present.

Because most acetone extracts of rubber have a yellow or brown color, it is recommended to perform at the same time the comparison test without $CuSO_4$.

PAPER–CHROMATOGRAPHIC SEPARATION AND IDENTIFICATION

Whatman paper No. 1 is used as the carrier of the stationary phase. For the detection of the antioxidants the paper must have been acetylated beforehand.

A. Guanidines.

The hydrochloric acid extracts Ia and Iba are applied to the paper, buffered at pH = 4. The chromatograms are formed by the ascending method, by means of water-saturated n-butanol, and are developed with 4 per cent sodium hypochlorite.

B. Amines.

The chromatograms are formed by the descending method by means of n-butanol, saturated with 0.5 N HCl, and are developed with a 0.2 per cent solution of ninhydrin in alcohol, containing 2 per cent of acetic acid and 0.5 per cent of cadmium acetate.

C. Amines.

The chromatograms are formed by the descending method by means of n-butanol, saturated with 0.5 N HCl, and are developed with 2 per cent copper sulfate, after resynthesis of dithiocarbamates by spraying a mixture of 50 ml. of ethanol, 50 ml. of carbon disulfide, and 2 ml. of triethylamine.

D. Methyl- and ethylaniline.

Before the separation, but after application to the paper, these amines are coupled with diazotized sulfanilic acid and neutralized. The chromatograms are formed by the descending method by means of n-butanol, saturated with 2 N ammonia. The spots are already colored.

E. Mercapto group.

The chromatograms are formed by the descending method by means of water-saturated n-butanol and are developed with a 5 per cent solution of bismuth nitrate in 0.5 N nitric acid. The dried chromatograms are observed in ultraviolet light.

F. Mercapto group.

The chromatograms on Whatman paper No. 1, buffered at pH = 10, are formed and developed as described under E.

G. Antioxidants with an amino group.

The chromatograms on completely acetylated paper are formed by the ascending method by means of a mixture of equal parts of ethanol and benzene, and are developed with a 4 per cent solution of benzoyl peroxide in benzene.

H. Phenolic antioxidants.

The chromatograms on completely acetylated paper are formed by the ascending method by means of a mixture of butyl acetate, pyridine, methanol, water (1:5:1:3), and are developed with Tollens' reagent.

I. Penolic antioxidants.

The chromatograms on completely acetylated paper are formed by the ascending method by means of a mixture of propanol-2, methanol, and water (3:3:2), and are developed with Millon's reagent.

DISCUSSION

A. If guanidines can be detected on chromatogram A of the HCl extract Ia, these accelerators were present in the rubber as such. The guanidine derivatives, identified in chromatogram A of the HCl extract Iba, originate from the corresponding thiourea derivatives.

B, C, and D. If one or more of these chromatograms have revealed the presence of amines, it is possible to investigate by means of color reactions (see K) whether these amines originate from dithiocarbamates or from thiuram sulfides.

However, complications caused by decomposition may occur. The N-substituted 2-benzothiazolyl sulfenamides, too, give rise to amines in Ia. In that case 2-mercaptobenzothiazole has to be found by the methods E and F. It is possible that the amines themselves are present in rubber.

E and F. Two chromatograms have to be made, one on an unbuffered strip, the other on a buffered (pH = 10) paper, in order to enable an unambiguous identification of 2-mercaptobenzimidazole and of 2-mercaptobenzothiazole.

H and I. The chromatograms of the phenolic antioxidants, too, have to be formed and to be developed in two ways, for a better result. In many cases, however, no unambiguous identification can be performed.

If a systematic investigation is carried out according to the outline given above, an unambiguous identification of the accelerators and antioxidants in rubber mixes and in vulcanizates of unknown composition can be performed in many cases, while in the other cases a satisfactory approximation can be achieved.

SUMMARY

Various difficulties in the identification of accelerators and antioxidants in rubber compounds are reviewed. A detailed procedure for the detection of four guanidine derivatives by paper chromatography is mentioned. The identification of diphenyl thiourea and diorthotolyl thiourea is also described.

A detailed procedure is given for the paper-chromatographic separation and identification of some mercapto-substituted heterocyclic compounds. The detection of these accelerators in rubber mixes and vulcanizates is also described.

A detailed procedure is given for paper chromatographic separation and identification of dithiocarbamates, which are used as ultra-accelerators in the rubber industry. These dithiocarbamates decompose in acid medium into secondary amines. The salts of these amines are better soluble in water than the dithiocarbamates, and are therefore more suitable for a paper-chromatographic separation. A method for the simultaneous detection of dithiocarbamates and thiuram sulfides is also described.

The paper-chromatographic separation and identification of various antioxidants is described. Because only few antioxidants can be separated by paper chromatography after coupling with diazotized arylaminosulfonic acids, it is preferable to separate these compounds, which are generally insoluble in water, by means of acetylated filter paper. The identification of antioxidants using acetylated filter paper is described.

A detailed procedure is given for the identification of accelerators and antioxidants in rubber mixes and vulcanizates of unknown composition.

ACKNOWLEDGMENTS

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THE QUANTITATIVE DETERMINATION
OF RUBBER CHEMICALS. II *

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Some time ago we published a series of methods for the quantitative analysis of rubber additives by conductometric titration[1]. They dealt mainly with the analytical chemistry of accelerators, especially with thiuram compounds, for which we have a great interest at the present time. Thiuram disulfides are capable of vulcanizing rubber (quinone dioximes, dinitroso compounds and dithiols react similarly with rubber[2]) with the simultaneous formation of the corresponding dithiocarbamates[3]. In the course of current investigations of the mechanism of vulcanization of rubber by thiuram disulfides with or without sulfur, on which we will report at a later date, we endeavored to find further possibilities for the quantitative determination of thiuram compounds. We have already reported[4] the conductometric titration of tetramethylthiuram disulfide with copper sulfate in presence of hydroquinone in a water-acetone solution. This analysis was also possible with dithiocarbamate present; in this case the dithiocarbamate was first titrated with acid. The method fails, however, when thiuram monosulfide is present because this also reacts with copper sulfate. The present paper deals with two determinations of tetramethyl-thiuram disulfide which are applicable when thiuram monosulfide is present.

THE QUANTITATIVE DETERMINATION OF TETRAMETHYL THIURAM DISULFIDE BY TRANSFORMATION INTO THIURAM MONOSULFIDE

Thiuram disulfides react with KCN to form thiuram monosulfides and KSCN as shown by von Braun and Stechele[5]:

$$(1) \quad >N-\overset{\overset{\displaystyle S}{\|}}{C}-S-S-\overset{\overset{\displaystyle S}{\|}}{C}-N< + KCN \rightarrow KSCN + >N-\overset{\overset{\displaystyle S}{\|}}{C}-S-\overset{\overset{\displaystyle S}{\|}}{C}-N<$$
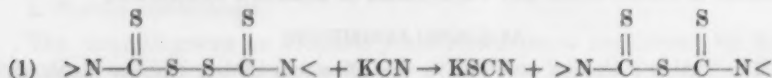
We sought to determine whether this reaction could be employed for the quantitative determination of thiuram disulfides and investigated the situation for tetramethylthiuram disulfide (TMTD).

For the execution of the analysis three possibilities could be considered, namely, (a) the reaction of TMTD with an excess of KCN and the conducto-metric back titration of the unreacted KCN with silver nitrate whereby the thiocyanate formed is determined simultaneously, (b) the reaction of TMTD with an excess of KCN and the argentometric titration of the thiocyanate formed after removal of the unreacted KCN with nitric acid, and (c) the determination of the tetramethylthiuram monosulfide (TMTM).

Intensive investigations have convinced us that immediately after the reaction with KCN, solutions of TMTD cannot be titrated conductometrically

with silver nitrate[6]. The TMTM which is formed during the reaction is adsorbed to an appreciable extent by the precipitates of AgCN and AgSCN, as is indicated slightly by their slight yellow color. The titration curves are thereby considerably changed. They are thus either not at all or not accurately evaluable, even though the conductometric titration, which we do not need to explain here, of a solution containing merely cyanide and thiocyanate is quite possible. Therefore the TMTM was extracted with benzene prior to the titration. Such pretreated solutions gave the expected titration curves, some of which are illustrated in Figure 1. Along segment I of these curves excess KCN is transformed to $K(Ag(CN)_2)$, along II AgCN and AgSCN are precipitated, and III indicates free silver nitrate in the solution. Although the points of intersection
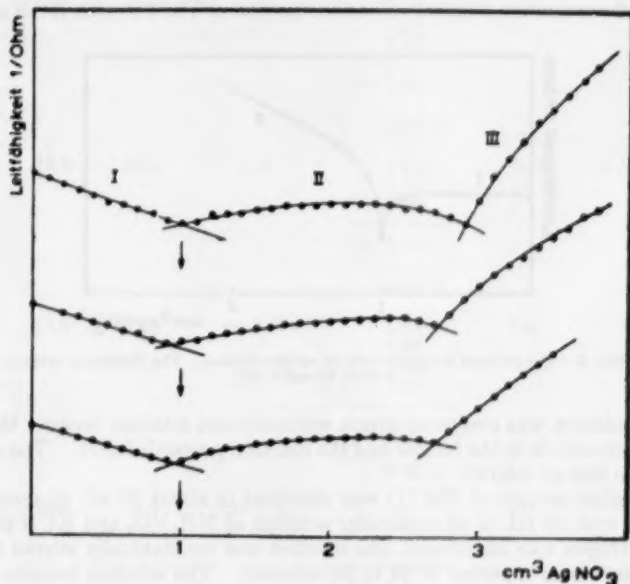
FIG. 1.—The ordinate is conductivity in reciprocal ohms. The abscissa is volume of silver nitrate in ml.

of the individual curves are well defined, which makes an accurate evaluation of the results possible, the amount of silver nitrate consumed at the first point of intersection indicates too little KCN, i.e., it gives the impression that too much KCN is used during the reaction with TMTD. Furthermore, the result of the analysis showed a distinct dependence on the molar ratio of the reactants. While the determination of the sum of excess KCN and of thiocyanate formed could be estimated accurately enough for all cases by means of the intersection of curves II and III, it was not sufficient for the calculation of the TMTD used up. Therefore the determination of TMTD was not based on the back titration of excess KCN. It was instead based on the determination of the thiocyanate formed.

For this reason the solution, which was extracted with ether or benzene in order to remove the TMTM formed, was titrated with nitric acid to a weakly

acid reaction and the liberated hydrogen cyanide driven off by heating the solution under a current of nitrogen. The subsequent conductometric titration with silver nitrate gave curves of the type shown in Figure 2. Along segment I AgSCN is precipitated, II indicates excess silver nitrate. Although the point of intersection of the two segments is in a deep notch, which is caused by foreign electrolytes, it is exactly the point of equivalence. This was proved by a separate set of experiments. The evaluation of the titrations, however, always indicated too high a consumption of silver nitrate; i.e., too much thiocyanate was found. Since TMTM is cleaved by alkalies (see later), a possible decomposition of TMTM by basically reacting alkali cyanide solutions existed under the reaction conditions, which might render the argentometric titration incorrect. Therefore work was done with potassium cyanide solutions which contained ammonium nitrate. For the reaction of TMTD with KCN a water-
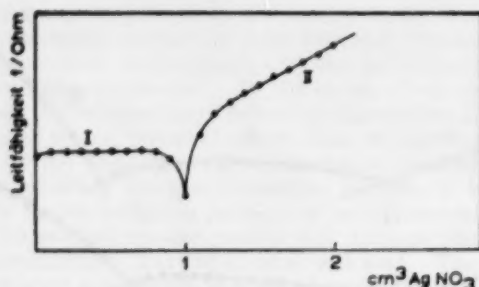
Fig. 2.—The ordinate is conductivity in reciprocal ohms. The abscissa is volume of silver nitrate in ml.

acetone solution was preferred over a water-alcohol solution because the disulfide is more soluble in the former and the reaction proceeds faster. The detailed procedure was as follows:

A weighed sample of TMTD was dissolved in about 20 ml. of acetone and added to with 10 ml. of an equimolar solution of NH_4NO_3 and KCN in water. While nitrogen was introduced, the solution was mechanically stirred at room temperature over a period of 20 to 30 minutes. The solution became yellow, indicating the formation of TMTM. This was followed by repeated extraction with ether and addition of nitric acid to give a weakly acid reaction. The liberated hydrogen cyanide was driven off by heating with the introduction of nitrogen. After this treatment the solution was sometimes extracted once more wtih benzene and was diluted in a volumetric flask to a specified volume. Aliquot parts were titrated conductometrically with silver nitrate of known concentration.

The results of such analyses are represented in Table I. It may be concluded since the deviations (in per cent) of the results from the calculated values are only slight and the 3 to 5 individual titrations of each experiment are in good agreement that the conductometric determination of thiocyanate is very reliable. However, in some cases (Experiments 1, 4, 9 and 10) the analytical errors are considerable. In Experiment 9 the cyanide excess obviously was not large enough; the amount of thiocyanate found was much too small. According to our experience the molar ratio of TMTD:KCN should be about 1:4 or preferrably smaller. It may be seen now that the analysis in general fur-

TABLE I

QUANTITATIVE DETERMINATION OF THE TETRAMETHYLTHIURAM DISULFIDE
AFTER THE REACTION WITH POTASSIUM CYANIDE

	1	2	3	4	5	6
Experiment number	Disulfide sample, mg.	KCN sample, mg.	Molar ratio disulfide: KCN	Found $AgNO_3$, ml.	Calcd. $AgNO_3$, ml.	Deviation of the mean value from the calculated value in %
1	18.0	19.5	1:4	0.05 N 1.36 1.34 1.31 1.23 Av. 1.31	1.5	−12.7
2	18.0	19.5	1:4	0.05 N 1.51 1.50 1.50 Av. 1.503	1.5	+ 0.2
3	18.0	13.0	ca. 1:3	0.05 N 1.44 1.44 1.46 1.46 Av. 1.45	1.5	− 3.3
4	18.0	13.0	ca. 1:3	0.05 N 1.4 1.4 1.4 Av. 1.4	1.5	− 6.6
5	12.0	19.5	1:6	0.05 N 0.96 0.97 0.95 0.95 Av. 0.96	1.0	− 4.0
6	12.0	13.0	1:4	0.05 N 0.98 1.00 0.98 0.97 1.02 Av. 0.99	1.0	− 1.0

TABLE I (continued)

	1	2	3	4	5	6
Experiment number	Disulfide sample, mg.	KCN sample, mg.	Molar ratio disulfide: KCN	Found AgNO₃, ml.	Calcd. AgNO₃, ml.	Deviation of the mean value from the calculated value in %
				0.05 N		
7	12.0	13.0	1:4	1.01	1.0	+ 2.0
				1.00		
				1.02		
				1.03		
				1.02		
				Av. 1.02		
				0.05 N		
8	12.0	13.0	1:4	1.0	1.0	− 1.0
				0.99		
				0.98		
				0.99		
				Av. 0.99		
				0.05 N		
9	12.0	6.5	1:2	0.6	1.0	−40.0
				0.6		
				0.6		
				0.6		
				Av. 0.6		
				0.025 N		
10	6.0	6.5	1:4	0.91	1.0	−11.1
				0.91		
				0.90		
				0.85		
				Av. 0.89		
				0.05 N		
11	12.0	19.5	1:6	1.0	1.0	0.0
				1.0		
				1.0		
				Av. 1.0		

nishes a somewhat low value for thiocyanate. It may be concluded from the results that the quantitative determination of TMTD when based on its reaction with KCN to give TMTM undoubtedly is not simple and some experience is required in order to do the analysis correctly. Therefore the method should be used only when special reasons call for it.

QUANTITATIVE DETERMINATION OF THIURAM DISULFIDE AS DITHIOCARBAMATE AFTER REACTION WITH DODECYL MERCAPTAN

Aliphatic mercaptans react with TMTD even in dilute acetone solution at room temperature to give alkyl disulfide and dithiocarbamate[7]. This reaction

may be used very conveniently and safely for the analysis of TMTD. Our reagent was dodecyl mercaptan, which reacts with TMTD as follows:

$$
(2) \quad >N-\overset{\overset{\text{S}}{\|}}{C}-S-S-\overset{\overset{\text{S}}{\|}}{C}-N< \; + 2CH_3(CH_2)_{11}-SH \rightarrow
$$

$$
CH_3-(CH_2)_{11}-S-S-(CH_2)_{11}-CH_3 + CS_2 + \; >N-\overset{\overset{\text{S}}{\|}}{C}-S-\overset{\overset{\text{H}}{}}{\underset{\text{H}}{N}}<
$$
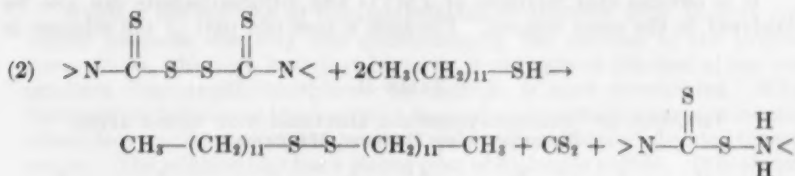
Analytical procedure.—To a solution of TMTD in pure acetone distilled over permanganate[8] an excess of a solution of known strength of dodecyl mercaptan in pure acetone is added. While introducing nitrogen in order to prevent oxidation of the mercaptan to disulfide by oxygen, the solution is gently heated for 20 to 30 minutes which is long enough to make the reaction go to completion. Without any further treatment the solution is titrated conductometrically with HCl at about 40° C. In the course of this titration the dithiocarbamate, which is formed according to (2), reacts to give CS_2 and dimethylammonium chloride. For the evaluation of the results it must be considered for each mole of TMTD that one mole of dithiocarbamate is formed, which upon titration consumes two equivalents of HCl. Another possible analysis involves the back titration of the excess dodecyl mercaptan with alcoholic iodine solution[9]. However, this method requires destruction of the dithiocarbamate with acid prior to the iodometric titration. It is also possible and often to be recommended to carry out both analyses consecutively in the same solution to give a double check on the TMTD determination without the need of any further operations. During the iodometric titration, which is performed preferrably at 0° C, the dodecyl disulfide generally precipitates partly in the form of fine needles[10].

The described double analysis of TMTD produces titration curves as shown in Figure 3. Curves *1* and *1'* were obtained by conductometric titration with HCl and *2* and *2'* represent the iodometric conductometric titration of the excess dodecyl mercaptan. The situation here is analogous to the conductometric titration of mixtures of mercaptobenzothiazole and dithiocarbamate[11].

The results of such double analyses are summarized in Table II. The iodometric titration of excess dodecyl mercaptan tends to give values which are too high, whereas the acidimetric titration of the dithiocarbamate gives
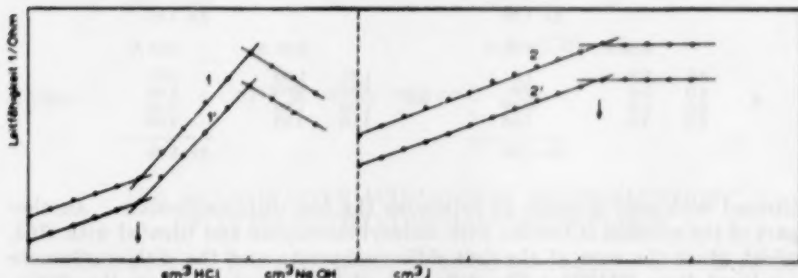
FIG. 3.—Conductometric titration curves for the double analysis of TMTD. The ordinate is conductivity in reciprocal ohms. The abscissa is volume of added reagents in ml.

excellent results.   In Experiment 5 it may be seen that the addition of TMTM did not influence the result.

It is obvious that mixtures of TMTD and dithiocarbamate can also be analyzed in the same manner.   For such a case one part of the solution is

TABLE II

TITRATION OF TETRAMETHYLTHIURAM DISULFIDE WITH IODINE AFTER REACTION WITH DODECYL MERCAPTAN

1	2	3	4	5	6	7	8
No.	Sample of disulfide, mg.	Calcd. HCl, ml.	Required HCl, ml.	Deviation of mean value from calcd. value in %	Milli-moles of mercaptan added	Calcd. iodine solution, ml.	Required iodine solution, ml.	Deviation of mean value from calcd. value in %
		0.1 N	0.1 N			0.05 N	0.05 N	
1	12.0	1.0	0.98		2.00	2.00	2.09	
	12.0	1.0	0.98		2.00	2.00	2.15	
	12.0	1.0	0.98	−1.0	2.00	2.00	2.18	+5.5
	12.0	1.0	0.99		2.00	2.00	2.19	
	12.0	1.0	0.97		2.00	2.00	2.06	
	12.0	1.0	1.04		2.00	2.00	2.00	
			Av. 0.99				Av. 2.11	
		0.05 N	0.05 N			0.025 N	0.025 N	
2	6.0	1.0	1.00		1.00	2.00	2.11	
	6.0	1.0	1.00		1.00	2.00	2.11	
	6.0	1.0	0.98	−1.4	1.00	2.00	2.15	+2.0
	6.0	1.0	0.98		1.00	2.00	2.02	
	6.0	1.0	0.97		1.00	2.00	1.88	
			—		1.00	2.00	2.00	
			Av. 0.986				Av. 2.04	
		0.05 N	0.05 N			0.025 N	0.025 N	
3	3.0	0.5	0.54		0.50	1.00	0.96	
	3.0	0.5	0.54		0.50	1.00	0.98	
	3.0	0.5	0.49	+3.0	0.50	1.00	1.07	+6.0
	3.0	0.5	0.51		0.50	1.00	1.18	
	3.0	0.5	0.51		0.50	1.00	1.07	
	3.0	0.5	0.50		0.50	1.00	1.09	
			Av. 0.515				Av. 1.06	
		0.01 N	0.01 N			0.01 N	0.01 N	
4	1.5	1.25	1.25		0.25	1.25	1.28	
	1.5	1.25	1.20	+2.3	0.25	1.25	1.20	+4.0
	1.5	1.25	1.38		0.25	1.25	1.43	
			Av. 1.28				Av. 1.30	
		0.05 N	0.05 N			0.05 N	0.05 N	
5	6.0	1.0	1.0		1.00	1.00	1.01	
	6.0	1.0	1.0		1.00	1.00	1.09	
	6.0	1.0	0.92	0.0	1.00	1.00	1.02	+3.0
	6.0	1.0	1.08		1.00	1.00	1.00	
			Av. 1.00				Av. 1.03	

titrated with acid in order to determine the free dithiocarbamate.   Another part of the solution is treated with dodecyl mercaptan and titrated with HCl, which gives the sum of the free dithiocarbamate and the dithiocarbamate produced from TMTD.   The difference of both titrations gives the dithiocarbamate which corresponds to TMTD.

FUNDAMENTAL FEATURES OF THE QUANTITATIVE
DETERMINATION OF THIURAM TETRASULFIDES

Whereas the reaction of tetramethylthiuram disulfide with dodecyl mer-
captan proceeds smoothly and quantitatively, the reaction of the thiuram
tetrasulfides, which we have just begun to investigate in the case of the very
sensitive dipentamethylenethiuram tetrasulfide, is more complicated. When
the tetrasulfide is allowed to react with dodecyl mercaptan in acetone, a reaction
takes place readily at room temperature and becomes faster at elevated temper-
atures. The solution also has a strong odor of hydrogen sulfide. It is obvious
that the initial reaction proceeds according to (3) and thereafter the polysul-
fidic bound sulfur of the tetrasulfide reacts with dodecyl mercaptan to give
hydrogen sulfide and dodecyl disulfide according to (4). However, the dithio-
carbamate, which is formed according to (3), will be in equilibrium, (5), with
hydrogen sulfide; and finally the carbon disulfide, which is formed in (3) and
(5) may also react to some extent with dodecyl mercaptan according to Re-
action (6). It appears that the tetrasulfide behaves as a mixture of TMTD
and sulfur. This argument becomes even stronger when the reaction of the
tetrasulfide with KCN is considered. Our experience up to the present time
has shown that in this reaction 3 moles of thiocyanate are formed for every mole
of tetrasulfide employed. We are not yet in a position to report details on the
quantitative determination of the tetrasulfide by means of KCN or dodecyl
mercaptan, respectively, because the investigation is still in process. However,
we can point out that the determination of free sulfur in presence of thiuram
compounds, which is very important, will be a part of the eventual proceedure.

$$
\begin{array}{l}
\text{(3)} \quad >\!N\!-\!\overset{\overset{\textstyle S}{\|}}{C}\!-\!S\!-\!S_2\!-\!S\!-\!\overset{\overset{\textstyle S}{\|}}{C}\!-\!N\!<\; +\; 2R\!-\!CH_2\!-\!SH \rightarrow \\[2ex]
\qquad S_2 + CS_2 + \; >\!N\!-\!\overset{\overset{\textstyle S}{\|}}{\underset{\underset{\textstyle H}{}}{C}}\!-\!S\!-\!N\!<\; +\; R\!-\!CH_2\!-\!S\!-\!S\!-\!CH_2\!-\!R
\end{array}
$$

$$
\text{(4)} \qquad S_2 + 4R\!-\!CH_2\!-\!SH \rightleftarrows 2H_2S + R\!-\!CH_2\!-\!S\!-\!S\!-\!CH_2\!-\!R
$$

$$
\text{(5)} \qquad >\!N\!-\!\overset{\overset{\textstyle S}{\|}}{C}\!-\!S\!-\!\underset{\underset{\textstyle H}{}}{\overset{\overset{\textstyle H}{}}{N}}\!<\; +\; 2H_2S \rightleftarrows CS_2 + 2\; >\!\underset{\underset{\textstyle H}{}}{\overset{\overset{\textstyle H}{}}{N}}\!\cdot HS
$$

$$
\text{(6)} \qquad CS_2 + R\!-\!CH_2\!-\!SH \rightleftarrows \overset{\overset{\textstyle S\!-\!CH_2\!-\!R}{\diagup}}{\underset{\underset{\textstyle S}{\|}}{C}}\!-\!SH
$$
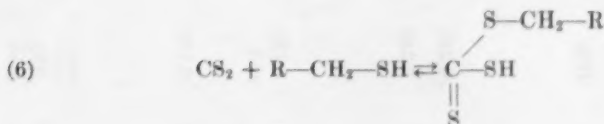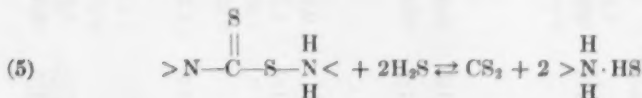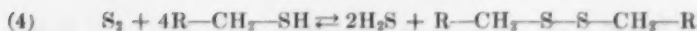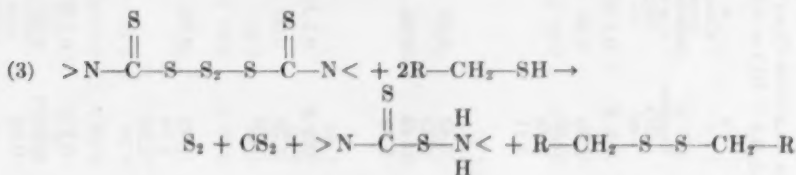
THE QUANTITATIVE ACIDIMETRIC DETERMINATION
OF TETRAMETHYLTHIURAM MONOSULFIDE

When a sodium hydroxide solution is added to an aqueous alcoholic solution
of tetramethylthiuram monosulfide (TMTM), the deep yellow color disappears
after only a short period of heating. Copper sulfate immediately produces a

TABLE III

The Titration of the Alkaline Cleavage Products of TMTM with HCl
(1 ml. 0.1 N HCl = 0.5·10⁻⁴ mole TMTM)

1 No.	Sample of TMTM, mg.	2 Added NaOH in milli-equiv.	3 Mol ratio TMTM : NaOH	4 Calcd. HCl, ml. 0.1 N	5 Required HCl, ml. 0.1 N	6 Calcd. extra consumption of HCl, ml. 0.1 N	7 Required extra consumption of HCl, ml. 0.1 N	8 % Deviation from expected Value	9 Remarks
1	10.42	0.25	1:5	3.5	3.43	1.00	0.93	− 7.0	Without pressure vessel
					3.42		0.92	− 8.0	
					3.48		0.98	− 2.0	
					3.41		0.91	− 9.0	
							Av. 0.94	Av. − 6.5	
2	10.42	0.245	1:5	3.45	3.42	1.00	0.97	− 3.0	With pressure vessel
					3.43		0.98	− 2.0	
3	10.42	0.240	1:5	3.40	3.40	1.00	1.00	0.0	
					3.39		0.99	− 1.0	
							Av. 0.985	Av. − 1.5	
4	5.21	0.122	1:5	1.72	1.70	0.50	0.48	− 4.0	Without pressure vessel
					1.70		0.48	− 4.0	
							Av. 0.48	Av. − 4.0	
5	5.21	0.122	1:5	1.72	1.72	0.50	0.50	0.0	With pressure vessel
					1.70		0.48	− 4.0	
					1.72		0.50	0.0	
							Av. 0.493	Av. − 1.3	
6	2.6	0.61	1:5	0.86	0.83	0.25	0.22	−12.0	Without pressure vessel
					0.84		0.23	− 8.0	
							Av. 0.225	Av. −10.0	

No.	Sample of TMTM, mg.	Added NaOH in milli-equiv.	Mol ratio TMTM: NaOH	Calcd. HCl, ml.	Required HCl, ml.	Calcd. extra consumption of HCl, ml.	Required extra consumption of HCl, ml.	% Deviation from expected value	Remarks
	1	2	3	4	5	6	7	8	9
7	2.6	0.61	1:5	0.05 N	0.05 N	0.05 N	0.05 N		With pressure vessel
				1.72	1.66	0.50	0.44	−12.0	
					1.70		0.48	− 4.0	
							Av. 0.46	Av. − 8.0	
8	2.6	0.72	1:6	0.05 N	0.05 N	0.05 N	0.05 N		With pressure vessel (at 40° C)
				1.94	1.88	0.50	0.44	−12.0	
					1.88		0.44	−12.0	
					1.86		0.42	−16.0	
					1.88		0.44	−12.0	
					1.88		0.44	−12.0	
							Av. 0.436	Av. −12.8	
9	2.6	0.96	1:8	0.1 N	0.1 N	0.1 N	0.1 N		With pressure vessel Excess alkali augmented
				1.21	1.23	0.25	0.27	+ 8.0	
					1.20		0.24	− 4.0	
					1.21		0.25	0.0	
							Av. 0.253	Av. + 1.3	
10	1.56	0.57	1:8	0.05 N	0.05 N	0.05 N	0.05 N		With pressure vessel Excess alkali augmented
				1.44	1.44	0.30	0.30	0.0	
					1.44		0.30	0.0	
							Av. 0.30	Av. ± 0.0	
11	1.30	0.48	1:8	0.05 N	0.05 N	0.05 N	0.05 N		With pressure vessel Excess alkali augmented
				1.21	1.19	0.25	0.23	− 8.0	
					1.20		0.24	− 4.0	
					1.23		0.27	+ 8.0	
							Av. 0.248	Av. − 1.3	

dark brown precipitate which presumably consists of copper thiocarbamates. A cleavage of TMTM takes place which may proceed according to (7) and (8).

$$(7) \quad >N-\overset{\overset{S}{\|}}{C}-S-\overset{\overset{S}{\|}}{C}-N< \ + \ 2NaOH \rightarrow$$

$$>N-\overset{\overset{S}{\|}}{C}-SNa \ + \ >N-\overset{\overset{S}{\|}}{C}-ONa \ + \ H_2O$$

$$(8) \quad >N-\overset{\overset{S}{\|}}{C}-SNa \ + \ >N-\overset{\overset{S}{\|}}{C}-ONa \ + \ 2NaOH \rightarrow$$

$$2 >N-H \ + \ S=C\overset{SNa}{\underset{ONa}{\diagdown}} \ + \ S=C\overset{ONa}{\underset{ONa}{\diagdown}}$$
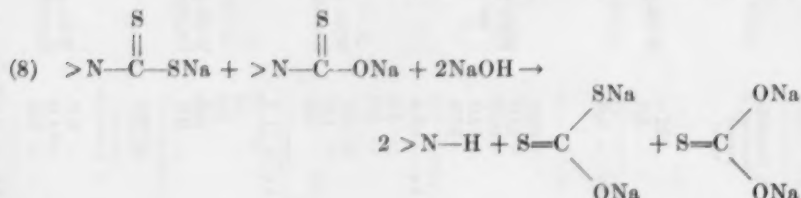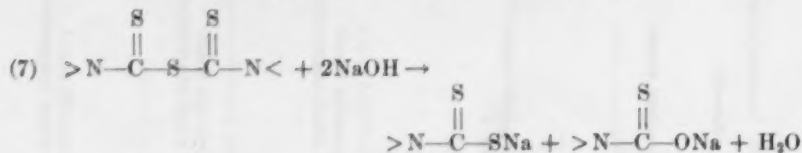
Initially 2 moles of NaOH are consumed per mole of TMTM while 1 mole of dithiocarbamate and 1 mole of monothiocarbamate are formed. Both compounds undergo further reaction according to (8) to give free amine and sodium dithio, as well as sodium monothiocarbonates. This is indicated by the dimethylamine which escapes when a solution of TMTM and NaOH is heated for a prolonged period. The complete reaction requires 4 moles of NaOH for every mole of TMTM. Now, when the solution of the TMTM is treated with an excess of NaOH, which incidentally is necessary for a quantitative reaction[12], the conductometric titration with HCl at the end of the reaction
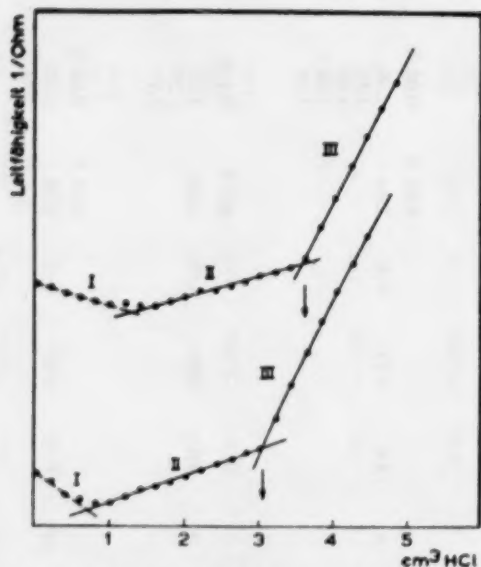
Fig. 4.—The ordinate is conductivity in reciprocal ohms and the abcissa is volume of HCl in ml.

gives titration diagrams as shown in Figure 4. Along I excess alkali is neutralized and if Reaction (8) is quantitative the thiocarbonates are destroyed along II and dimethylamine is transformed into its hydrochloride. If (8) does not proceed quantitatively, the thiocarbamates from reaction (7) are destroyed and simultaneously a corresponding amount of dimethylamine forms a salt with the acid. Along III excess alkali* is in the solution. The location of the point of intersection between I and II will depend on the progress of Reaction (8): the further (8) has progressed, the less acid will be consumed along I.

The second point of intersection between II and III always will appear in the same location, no matter how quantitatively Reaction (8) proceeded, whereas the first point of intersection of the titration curve always is uncertain. It is concluded that the titration with acid determines the total alkali which is found as free base (excess) + bound base (thiocarbamate and thiocarbonate, respectively, and an additional amount of acid is consumed by the dimethylamine which is liberated according to (8). This extra acid is equivalent to the dimethylamine and therefore equivalent to the TMTM.

TABLE IV

TITRATION OF ALKALI TREATED TMTD WITH ACID

Entire charge, mg.	Vol. NaOH added, ml.	Reaction time, hours at 60° C	Starting disulfide per titration, mg.	Vol. 0.05 N HCl equivalent to the formed dimethylamine, ml.		% Deviation
				Calcd.	Found*	
120.2	25 0.1 N	8	6.0	1.0	0.84	−16
					0.82	−18
120.2	30 0.1 N	8	6.0	1.0	0.86	−14
					0.84	−16
120.2	30 0.1 N	16	6.0	1.0	0.92	− 8
					0.90	−10
60.1	20 0.1 N	18	3.0	0.5	0.41	−18
					0.405	−19
60.1	10 0.2 N	18	3.0	0.5	0.40	−20
						−23

* This is the difference between consumed HCl and added NaOH. (1 mole TMTD = 2 moles dimethylamine = 2 moles HCl.)

Table III represents a series of results of cleavages of TMTM with alkali. These reactions were performed at 40° C in a relatively dilute solution (not too high a pH value) thus suppressing reaction (8) as far as possible. The last column of the table contains short notes on the respective reaction conditions. The reactions which were carried out in a pressure vessel gave better results than those in open flasks because in the latter cases some loss of amine could not be avoided (compare the deviations, which for experiments 1, 4 and 6 always are negative). A rather generous excess of alkali should be used, especially when small samples are analyzed (1:8), compare column 3). The average deviations in any case from the expected values under optimal conditions (large excess of alkali, pressure vessel) for samples as little as 1.3 mg. did not exceed ±1.5%. We therefore consider the results to be satisfactory and it is justified to assume that the cleavage of TMTM proceeds according to the Equations (7) and (8). The titration in Experiment 8, was performed at 40° C. It is evident that due to this temperature some amine escaped which caused quite large negative deviations. For this reason the acidimetric conducto-

* Translator's note: this is probably an error, instead of *excess alkali* read *excess acid*.

metric titration during the determination of TMTM should be carried out at temperatures which do not exceed room temperature.

It remains uncertain whether the cleavage of TMTM with alkali can be applied as an analytical method in every instance. This will depend on the special circumstances under which the determination of the TMTM has to be done. Thiuram disulfides as well as dithiocarbamates should not be present. TMTD is also cleaved by alkalies, although the reaction is not nearly as well understood as with TMTM. Table IV illustrates this with results of some alkali cleavages of TMTD. The acid consumption in the course of the conductometric titration is always much smaller than that theoretically required by the 2 dimethylamine fragments of the TMTD. These difficulties might be eliminated, however, if after treatment of the solution with dodecyl mercaptan the resulting dithiocarbamate and TMTD were destroyed with acid and the acid solution was extracted with ether or benzene in order to isolate TMTM. Subsequent analysis probably is not affected by the excess dodecyl mercaptan and even if it should have an effect, it could be oxidized to the disulfide prior to the analysis.

SUMMARY

A quantitative method for the determination of thiuram compounds has been reported. It has been found that tetramethylthiuram disulfide is converted quantitatively to thiuram monosulfide if it is treated with an excess of potassium cyanide. The thiocyanate, which is also formed, can be determined by argentometric conductometric titration. The execution of the analysis requires a good deal of experience. The conductometric titration with acid of the dithiocarbamate, which is formed by the reaction of TMTD with dodecyl mercaptan is much simpler. This method permits a double determination of the thiuram disulfide in which the excess dodecyl mercaptan is titrated conductometrically with alcoholic iodine solution. Solutions of dipentamethylene thiuram tetrasulfide behave like mixtures of tetramethylthiuram disulfide and sulfur. Also thiuram monosulfide and thiuram disulfides are cleaved by alkali and for the monosulfide a stoichiometric course of the reaction has been established.

During our studies on the vulcanization of rubber with thiuram disulfides we have found conductometric analysis procedures to be very useful for the investigation of vulcanization extracts. We will report on this in the near future.

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[4] Scheele and Gensch, *Kautschuk u. Gummi* 6, WT147 (1953).
[5] von Braun and Stechele, *Ber.* 36, 2280 (1903).
[6] On the conductometric titration of cyanides and thiocyanates compare Kolthoff, *Z. anal. Chem.* 61, 229, 332 (1922). The normality of potassium cyanide solutions must be determined argentometrically since even analytically pure potassium cyanide may contain some potassium carbonate. The point of intersection of curve segments I and II in Figure 1 is determined.
[7] Craig et al., *J. Polymer Sci.* 6, 1 (1951).
[8] The stability of solutions of TMTD in acetone is limited. Decomposition occurs rapidly in boiling acetone to form dimethylamine. Therefore, it is recommended to analyze immediately those solutions of TMTD which might contain acetone. Extraction of TMTD vulcanizates with acetone in a Soxhlet is not recommended, if it is planned to determine the TMTD content of the vulcanizate.
[9] Solutions of iodine in alcohol are reasonably stable only if the alcohol is very pure. It is advisable to check the normality periodically with standard thiosulfate solution.
[10] The dodecyl mercaptan content of the acetone solutions must be determined iodometrically. This may be done by conductometric titration at 0° C.
[11] Scheele and Gensch, *Kautschuk u. Gummi* 6, WT147 (1953).
[12] The reaction has to be carried out in such a manner that no dimethylamine can escape. The use of a pressure vessel is recommended.

TIRE CORD FATIGUE AND FATIGUE TESTING *

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INTRODUCTION

Examination of failed tires shows that fatigue failure mostly occurs on the inner plies, i.e., those subjected to compressive bending stress when the sidewall is bent. Continual flexing of the sidewall leads to a reduction of tensile strength of the cords until eventually the sidewall breaks up and the tire fails[1,2]. This fatigue failure is essentially a function of the complex structure of the tire. When a tire is inflated all the cords are in tension throughout and when it is loaded the sidewall of that part of the tire in contact with the ground is bent so that some of the cords are subjected to relieved tensile stress or, if the deflection is very great, to compressive stress, and the rest of the cords to tensile stress. When the cord goes from tension to compression it tends to collapse but this is complicated by the constraining action of the surrounding rubber. If the tire now rotates the cords will be subjected to alternate tension and quasi-compressional stresses leading to ultimate failure.

Fatigue performance is usually assessed by the average mileage to failure of the tire. If the plies of a tire are tested by extracting cords before failure occurs it can be shown that there is a progressive loss of strength of those plies undergoing compression. It has been asserted that this drop is linear with tire life and is greatest on the innermost ply, i.e., at the point of greatest compression[2]. The outer plies undergo a cyclic increase and decrease of tension at constant stress and although there is a small reduction in breaking strength, this does not usually contribute to tire failure[2].

It has been stated that the tensile strength of a textile in cord form, with adequate twist inserted, is a good criterion of its fatigue resistance when incorporated within a tire[3]. Obviously, the greater the strength of the cord, the longer it will flex before the reduction in tensile strength leads to failure of the tire.

A considerable amount of work has been published on the development of laboratory testers designed to evaluate the fatigue life of tire cord[4-15]. Most of these may be classified into two types, namely "in rubber" and "raw cord". As it is extremely difficult to subject a cord surrounded by air to the complex compressive forces experienced by a cord surrounded by rubber, most of the "raw cord" testers tend to be of the tension fatigue type. Although they produce a type of fatigue failure of the cord, it rarely correlates with tire performance[6]. If the mechanism of the failure is not the same as that producing failure in a tire then the results may be very misleading and may lead to the rejection of a cord construction which might give a good performace if incorporated in a tire. Of the "in rubber" testers the "Goodrich Compression Fatigue Tester" has been shown to correlate well with actual service conditions[2,10].

Tire cords made from the manmade, synthetic fibers normally require bonding agents to stick them to rubber. When the tire is flexed the bond is strained. If the bond fails then the cord will quickly fatigue due to relative movement of cord and rubber. Conversely, if the cord fatigues then failure of the bond will quickly follow. This interrelationship between bond and cord can often lead to misinterpretation of results, a low fatigue life being attributed to a cord when
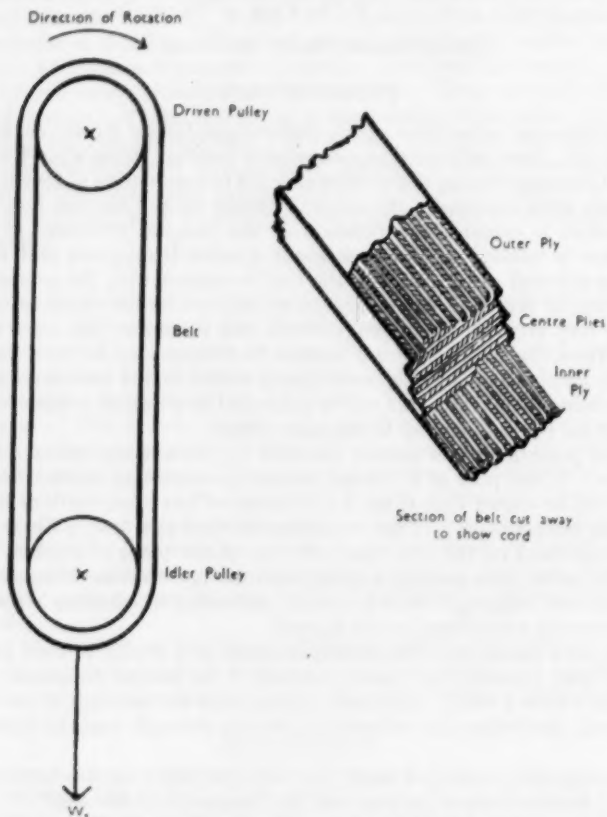
FIG. 1.—Dunlop tire cord fatigue tester. Principle of test.

the break up is actually due to a premature failure of the bond. The amount of bonding agent deposited on the cord has also been shown to affect fatigue life, an excessive quantity reducing the flex life[10,13,16].

NEW FATIGUE TESTER FOR TEXTILE CORDS

Based on the premise that the best way to test a cord is to run it in a tire, a fatigue tester has been devised which employs a plied structure similar to that obtaining in a tire[2].

A cord-rubber testpiece is built up consisting of an endless belt of rubber made up of four plies of rubberized cord, the inner and outer of which lie along

the belt axis. The belt is run under controlled conditions around pulleys in such a manner that the cord of the inner ply undergoes compression when passing around the pulleys.

Figure 1 illustrates the principle of the test and Figure 2 is a photograph of the test machine. The belt is constructed on a former, the test plies being wound on in a helix. After building, the belt is transferred to a cylindrical airbag and cured in a mold, thus simulating tire molding conditions. The two plies in the center, at 90° bias, are packing plies which ensure that the test plies undergo compression and extension, respectively, when they go around the pulley. The belts are 1 inch wide and 0.187 inch thick in their finished state.
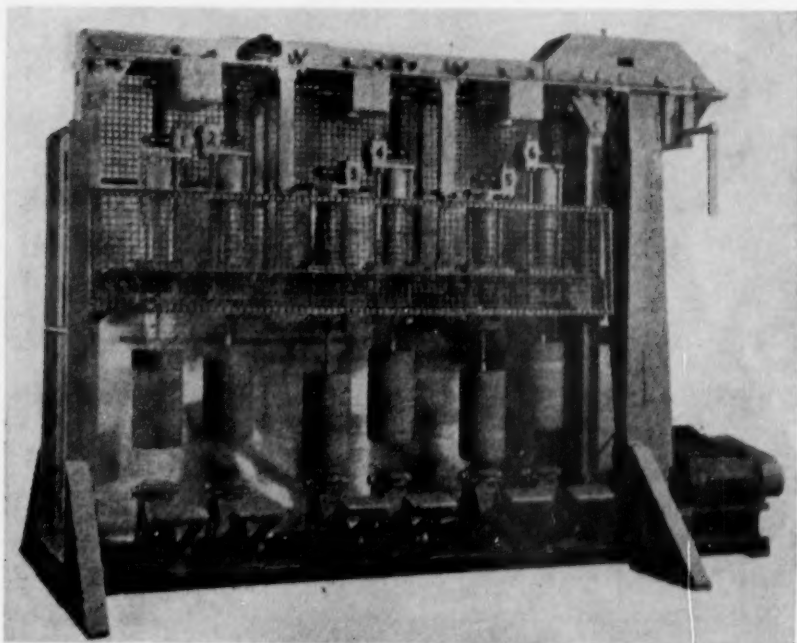
Fig. 2.—Dunlop tire cord fatigue tester.

They are rotated by the driven top pulley and tension is applied by a weight hanging on the bottom pulley. The angle of flex and hence the degree of compression may be altered by changing the pulley diameter. Load on the specimen also may be varied and, by changing the number of ends per inch wound on for the test plies, the load per cord is altered. Normally the number of ends per inch used is of the same order as that used in the sidewall of the tire.

Figure 3 shows how the loss of strength of a 2/1100 denier rayon cord varies with load when the flex angle is kept constant. On the other hand, a sharp angle of flex and high loading on the belt produce test conditions leading to ply looseness on the outer ply before fatigue failure occurs on the inner ply. This often happens in tire service where outer ply and tread looseness may occur in tires which are run under low inflation pressures accompanied by considerable overloading. Hence conditions of test may be adjusted to match tire conditions.

Compression fatigue of the cords is measured by the drop in tensile strength of the inner ply after running for a given number of flex cycles. Tension fatigue may be measured by finding the change in strength of cords from the outer ply. The belt, after running, is cut and the plies are stripped down. Single cords are then extracted and placed on a frame to condition before testing. After a little experience, it is found that cords may be extracted without damage. The cords nearest the edge of the specimen are ignored to avoid any spurious edge effects. It is found that one belt will yield enough for ten 10 inch test speci-
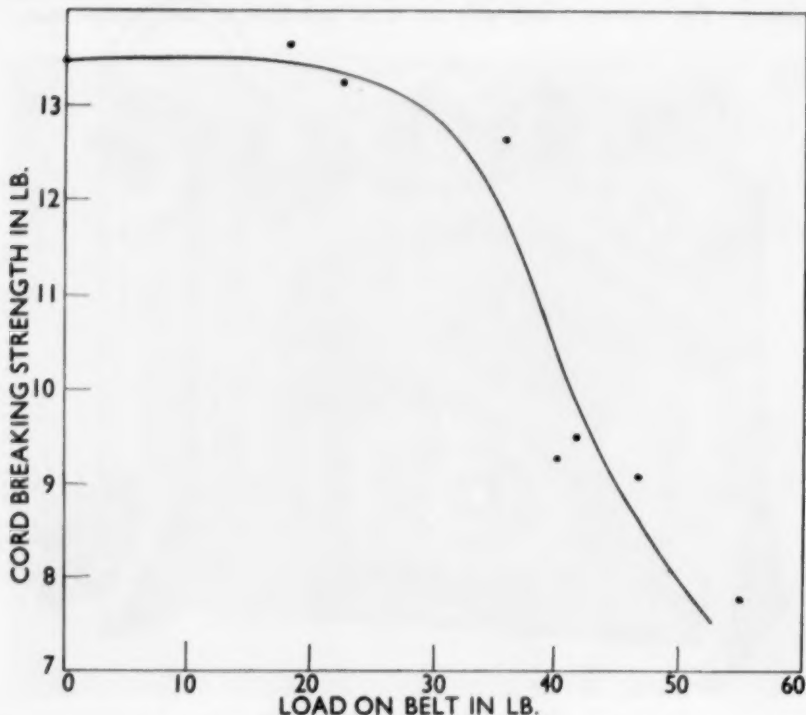
Fig. 3.—Effect of loading on flex life of a 2/1100 den. rayon tire cord.

mens. Extension of the belt can be measured during running and hence cord growth under dynamic conditions assessed. Full details of cord extensibility changes during running also can be recorded.

TEXTILE CORD FATIGUE TESTING

Influence of twist.—It has been shown that cord twist has an influence on the rate at which a cord will fatigue under compressive stress in a tire[12]. Two 2/1650 denier cords were made up in twist constructions 13.0 Z turns per inch singles, 13.0 S turns per inch folding and 11.5 Z turns per inch singles, 10.0 S turns per inch folding, from the same sample of rayon yarn and dipped in the same bath of resorcinol-formaldehyde-latex dip. These were then compared on
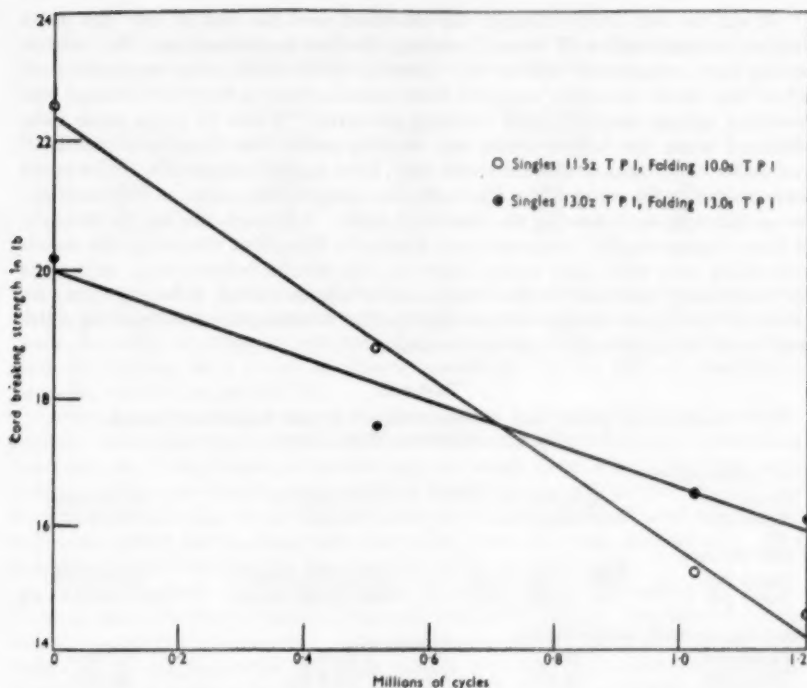
FIG. 4.—Effect of twist on the flex life of a 2/1650 den. rayon tire cord.

the belt fatigue tester under identical flex conditions. The test data are shown in Figure 4. Fatigue resistance is seen to be very dependent upon cord twist and loss in strength is approximately linear with flexing time. Some similar data for cotton cords are given in Table I. For this series of tests the load per cord used was higher than that used for the cords in Figure 4 and hence the relative strength losses are greater. The three cords compared are:

(1) A standard cotton cord.
(2) A cord of similar construction but twisted to give maximum strength.
(3) A twisted roving cord.

A twisted roving cord is made by twisting two or more rovings together without draft. This is a method of twisting cotton to give a very strong, low extensibility cord.

TABLE I

EFFECT OF TWIST AND CONSTRUCTION ON THE COMPRESSION
FATIGUE LIFE OF COTTON TIRE CORD

Cord construction	Twist/inch	Breaking strength before flexing	Breaking strength after flexing for 0.42 ×10⁶ cycles	
			Inner ply	Outer ply
3/4/16.7's	9.0S/18.8Z/14.6Z	22.8 lb.	16.0 lb.	21.4 lb.
3/4/16.7's	5.0S/7.0Z/14.6Z	25.0 lb.	0	—
2/4.25 hank	8.7S/4.1Z	17.0 lb.	0	—

It will be seen that, although the standard cord has lost 50 per cent of its original strength after 24 hours' running, the low twist cord and the twisted roving have completely broken up. Results of the same order were obtained when tires made of similar material were tested. Only a very low mileage was recorded before complete cord breakup occurred. Table II gives some data obtained when the fatigue tester was used to prove that these same cords, if run under conditions of tension stress only, have a good fatigue life. The cords were built into the outer ply of the belts, the compression stress on the inner ply being taken in each case by the standard cord. Although the loss in strength of these high strength, low twist cords is greater than that shown by the standard cotton cord when used as the outer ply, the results indicate that, so long as the material is used only under conditions of tension stress, advantage may be taken of the higher strength obtainable by that construction thus making a tire with good casing strength and performance.

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TABLE II

EFFECT OF TWIST AND CONSTRUCTION ON THE TENSION FATIGUE
LIFE OF COTTON TIRE CORD

</div>

Cord construction			
Outer ply	3/4/16.7's	3/4/16.7's	2/4.5 hank
Inner ply	3/4/16.7's	3/4/16.7's	3/4/16.7's
Twist per inch			
Outer ply	9.0S/18.8Z/14.6Z	5.0S/2.0Z/14.6Z	8.7S/4.1Z
Inner ply	9.0S/18.8Z/14.6Z	9.0S/18.8Z/14.6Z	9.0S/1.88Z/14.6Z
Breaking strength, before flexing			
Outer ply	22.8 lb.	25.0 lb.	17.0 lb.
Inner ply	22.8 lb.	22.8 lb.	22.8 lb.
Breaking strength after flexing 0.42×10^6 cycles			
Outer ply	20.5 lb.	17.2 lb.	13.7 lb.
Inner ply	15.1 lb.	14.7 lb.	15.5 lb.

Nature of fatigue.—Correlation with tire performance was first established, within the limits that an accelerated laboratory test could be expected to give, by comparing the order in which the test placed the cords in current use with their rating in actual service. Having shown that the ratings agreed, a series of tests on cotton cords were run in an endeavor to investigate the mechanism of fatigue.

Cords were flexed for different periods and tested by a number of standard tests. The fatigued cords were tested for yarn and cord breaking strength to determine the relative rates of loss of strength with flexing. The change in staple length and amount of fiber breakup in the cotton during fatigue were estimated from Baer sorter analyses of samples taken from the fatigued plies[17]. The extent and nature of fiber damage were assessed by swelling the fibers in caustic soda and staining with Congo Red[18,19]. Fluidity tests on samples taken from fatigued plies were used to given an indication if any molecular or structural damage takes place during fatigue[20]. 3/4/16.7's cotton cord was used throughout the test. The cord was carefully examined to ensure that it was uniform and free from first folding or yarn knots. Standard belts were then constructed, the test plies being wound 24 ends per inch.

Sets of the belts were run for 0.07, 0.14, 0.28, and 0.56×10^6 flex cycles, respectively. After running, the test plies were stripped from the belts and

TABLE III

CHANGE IN BREAKING STRENGTH OF COTTON TIRE CORD AND
CONSTITUENT YARNS AFTER FLEXING

Flexes, cycles ×10⁶	Cord breaking strength lb. (av. of 20)	Range, lb.	Yarn breaking strength g. (av. of 50)	Range, g.
0	23.3	2.5	802	270
0.07	16.7	1.5	604	320
0.14	17.4	2.3	560	320
0.28	16.5	2.1	461	700
0.56	14.3	1.8	550	460

samples were taken from the inner plies. A belt that had not been flexed was
also pulled down and cords were extracted in a similar manner. The extracted
cords, including a sample of raw cord, for use as a control, were then derubber-
ized, by heating for 2 hours in diphenyl oxide at 159° to 160° C, washing in
benzene, and drying at 100° C.

After derubberizing, some of the cords were tested for breaking strength,
and the remainder were broken down into their three first foldings, one folding
from each set being chosen at random and one single yarn being taken from each
folding. This was done by suspending a weight on one end of the cord and un-
folding from the other end. These yarns were then untwisted, well mixed, and
sufficient cotton for the fiber tests was taken from the tufts so obtained. The
remaining yarn was used for the yarn breaking strength tests.

Table III shows the results obtained for yarn and cord breaking strengths.
Tests of the cord show a steady drop with increasing fatigue, the range for each
sample being fairly constant. Yarn tensile strengths also give a steady but
larger drop and the range for each sample increases with increased fatigue,
indicating that some yarns are damaged more than others as fatigue progresses.
This was confirmed when breaking down the belt that had flexed for 0.56×10^6
cycles. It was observed that some of the foldings and yarns were cracked and
damaged and the force used during separation was, on occasions, sufficient to
break them. In a damaged folding, one yarn could be broken in as many as
four places while the other three were undamaged. Hence the value for yarn
tensile strength after 0.56×10^6 flexes is biased, owing to the exclusion of these
damaged yarns.

The measurements taken from the Baer sorter diagrams are shown in
Table IV. A brief description of the terms used in examining the diagrams is
given below[17].

Maximum length.—The length of the longest fiber.

Mean length.—The average fiber length of the sample.

Effective length.—This may be defined as corresponding to the upper quartile
of that portion of the distribution in which all fibers are longer than one half of

TABLE IV

CHANGE IN FIBER PROPERTIES OF COTTON TIRE CORD AFTER FLEXING.
READINGS TAKEN FROM BAER SORTER DIAGRAM

Flexes cycles × 10⁶	Maximum length × 1/32 in.	Mean length × 1/32 in.	Effective length × 1/32 in.	Percentage short fibers	Percentage dispersion
0	62	32	46	28.6	32.6
0.14	56	28	42	36.6	33.4
0.28	56	27	41	44.6	29.3
0.56	58	27	41	46.6	31.5

the effective length.   It was originally devised as a means of obtaining a measure, equivalent to the staple length as given by a cotton broker, when hand stapling.

Percentage short hairs.—This includes all hairs short enough to be excluded from the measurement of effective length.

Percentage dispersion.—This gives a measure of the uniformity of hair length, independent of the absolute length.

Figure 5 shows the sorter diagrams obtained after combining and Figure 6 shows fiber lengths plotted as frequency polygons, the hairs in the diagram being
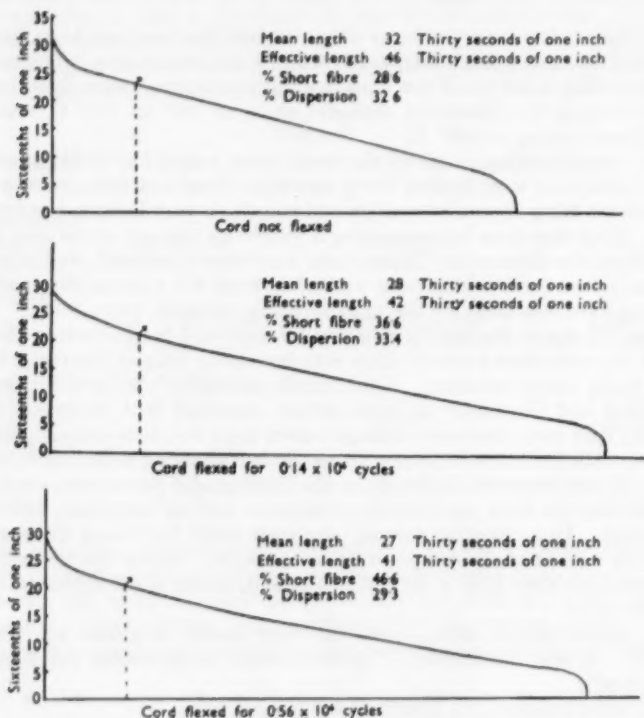
FIG. 5.—Baer Sorter diagrams of flexed cords.

divided into classes of two sixteenths of an inch.   Those shown are from the new unflexed belt and the belts flexed for 0.14×10^6 and 0.56×10^6 cycles, respectively.

Maximum length, mean length, and effective length all decrease more in the initial stages of fatigue than in the later stages, while the number of short hairs increases.   Dispersion stays fairly constant, indicating that all fiber breakup is distributed over the whole range of fibers in the sample.   The measured decrease in length may be shown to be unduly large during the early stages of fatigue because damaged fibers were broken during the combing.

An empirical formula[21], found to be accurate to about 10 per cent, for cal-

culating yarn strength from the staple length of the fiber is:

$$S = 6840 \ (1 \pm 0.11a \pm 0.01b)/c$$

where S = yarn strength in grams.

    a = length of staple greater or less than 1 inch, expressed in 1/16th inch.

    b = difference in count above or below 28's.

    c = count of yarn.

Using effective length as a measure of staple length this formula gives a value of $S = 775$ g. for raw cord and $S = 680$ g. for cord fatigued for 0.56×10^6 flexes. This raw cord figure is in reasonable agreement with the measured
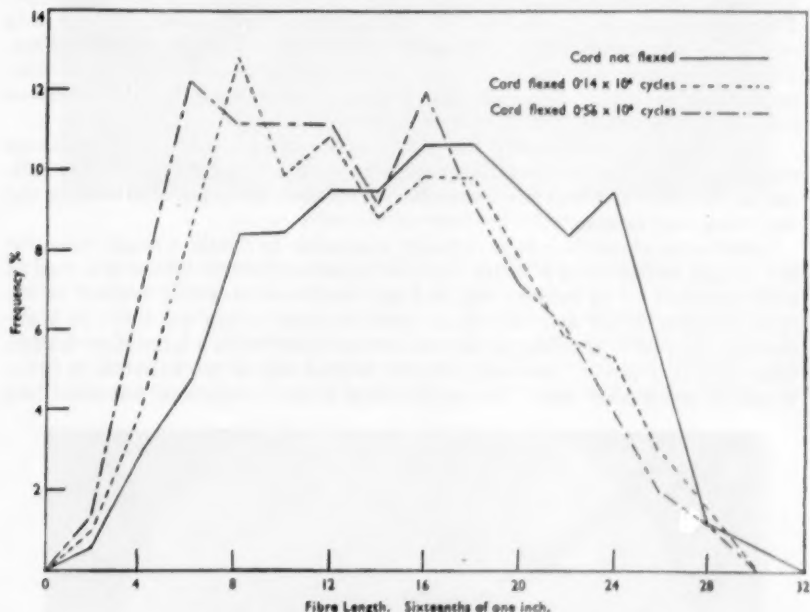
FIG. 6.—Frequency polygons of fiber lengths of flexed cords.

value but the calculated value after fatigue is too high. This would indicate that actual fiber breakup, as shown by change in length in a sorter analysis, is not the only damage due to fatigue.

In the Congo Red test, fibers are usually classified:

    (1). Normal: undamaged.

    (2). Abnormal: cracks associated with the presence of abnormalities in the fiber.

    (3). Bruised: cuticle rubbed allowing the secondary cellulose to protrude.

    (4). Torn: secondary cellulose torn and stained.

The number of fibers falling into the various groups is then expressed as a percentage of the whole. The figures obtained are shown in Table V. Norm-

TABLE V

CHANGE IN FIBER PROPERTIES OF COTTON TIRE CORD AFTER FLEXING. READINGS
TAKEN FROM CONGO RED SWELLING TEST AND FLUIDITY TEST

Flexes, cycles × 10^6	Normal, %	Abnormal, %	Bruised, %	Torn, %	Fluidity, reciprocal poises
0	68	14	14	4	4.9
0.14	55	32	9	4	5.2
0.56	43	15	32	10	4.7

ally in testing for mechanical damage most of the damaged fibers fall into the
bruised and torn category, but in the sample flexed for 0.14×10^6 cycles there
was a very high proportion of fibers which showed a very slight cracking along
the spiral convolutions of the fiber. Figure 7 is a photograph of one such fiber.
The damage may be the start of fiber breakup due to mechanical flexing or it
may have been caused by a very gentle abrasive action of fiber against fiber.
This fine cracking eventually develops into bruising normally associated with
mechanical damage. Figures 8 and 9 show typical bruised and torn fibers
taken from the sample flexed for 0.56×10^6 cycles.

The results of the fluidity test also are shown in Table V. There is no
significant difference in the fluidity figures obtained and there is thus no indi-
cation from this test that any molecular degradation takes place, at least in the
early stages of fatigue.

Discussion of results.—It is virtually impossible to obtain a single value for
the fatigue resistance of a textile tire cord material. Performance of a cord in
a tire depends on its construction and the conditions of flexing depend on the
type and size of tire and vary from point to point within the tire. It is ex-
tremely difficult to simulate all the conditions of service in a laboratory fatigue
tester and it is usually necessary to alter at least one of the variables in order
to get an accelerated test. The acceleration of the textile cord test described
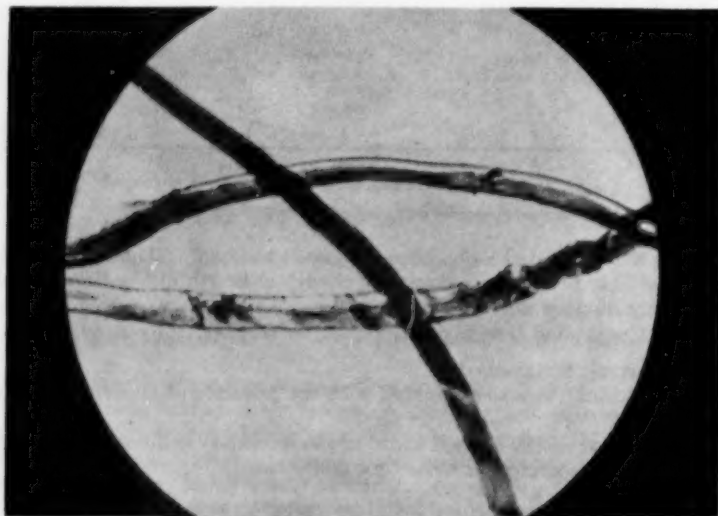
FIG. 7.—Fibers from cord flexed 0.14×10^6 cycles.
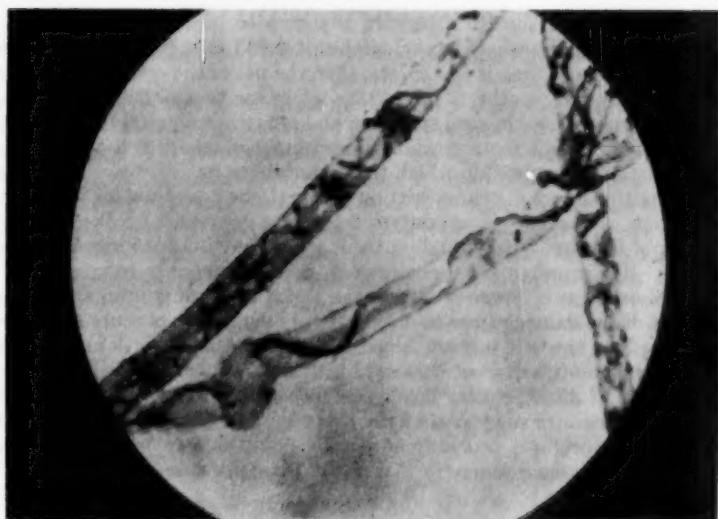
Fig. 8.—Fibers from cord flexed 0.56 ×10⁴ cycles.

above is obtained by using a high angle of flex. Hence it probably gives values close to tire performance where the angle of flex is high, but which will be biased where those conditions do not prevail. In Figure 4, for example, the comparative test of two 2/1650 denier rayon cords, the one with twists 13.0 Z turns per inch in the singles and 13.0 Z turns per inch in the folding and the other with 11.5 Z turns per inch in the singles and 10.0 S turns per inch in the folding, the
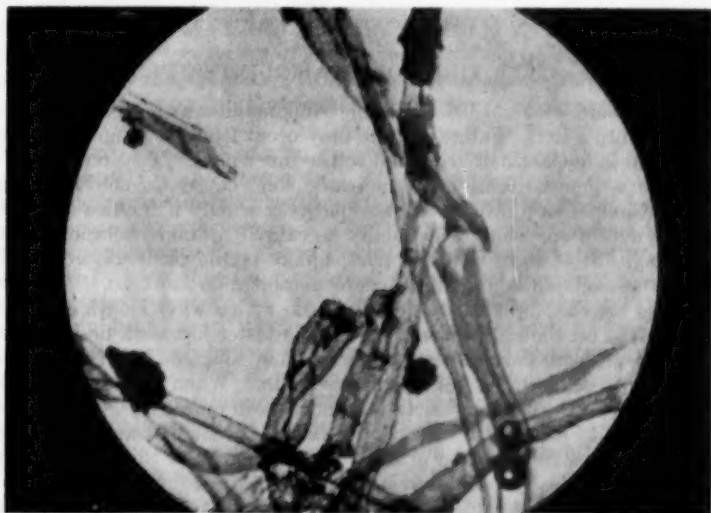
Fig. 9.—Fibers from cord flexed 0.56 ×10⁴ cycles.

fatigue resistance of the 13 × 13 cord is shown to be better. However, this may hold for a car tire where flex is high but if the 11.5 × 10.0 cord were used in a giant tire, where flexing is less severe, then the life of the cord would probably be of the same order as the 13.0 × 13.0 cord in car tires and advantage might then be taken of the extra cord strength, and hence extra casing strength, given by the lower twist. A figure for fatigue resistance of a cord is thus meaningless unless the stress range within which the material has been flexed is quoted also.

When a tire is run the same portion of the tire is flexed for each revolution, the position of the line of maximum flex being governed by the design and geometry of the tire. It is usually at this point that the cord breaks when the tire fails. Hence only a small portion of a cord extracted from a partially run tire, will show signs of progressive damage and if the cord is from a failed cover the extent of the damage from failure is usually enough to obscure all evidence.

The cords in the belt test are flexed along their whole length and damage is uniform throughout. Hence more cord is available for a detailed examination of the extent of damage after flexing. Fiber and yarn tests on cotton cords flexed in this manner suggest that fiber damage starts early in the flex life of the cord. The origin is probably at a weak point in the cord and subsequent damage would be more severe in this region than elsewhere.

Fully Extended   Closed
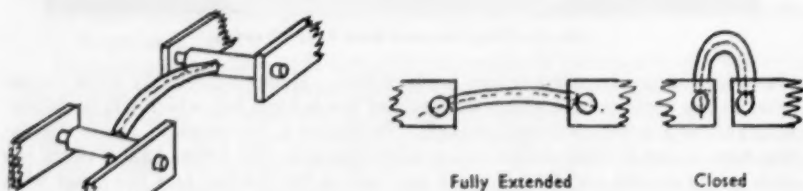
FIG. 10.—Wire tire cord fatigue tester.

STEEL TIRE CORD FATIGUE TESTER

Steel tire cord does not behave in the same manner as textile cord when incorporated into a tire. Fatigue failure may occur from both tension and compression and is not normally confined to the inner plies. Tension fatigue may be tested on a dynamic tension fatigue tester which causes the cord to flex under tension. Compression fatigue will normally occur only if the tire is subjected to a large deflection, which will usually be caused by underinflation or heavy overloading. Steel cords on inner plies, unlike textile cords, do not tend immediately to collapse when subjected to compression; instead, they tend to buckle, and the cord assumes a sine wave form with a wave length of about 0.5 in., dependent on the size of cord. A fatigue tester has been designed which flexes a wire enclosed in a rubber cylinder 1.125 in. long and 0.187 in. diameter. Frequency of oscillation is 1800 cycles per min. When flexed the specimen assumes a rounded shape similar to the buckle seen on a tire. The number of flexes required to fatigue the specimen to failure is recorded and the end point is determined by the detection of the change of shape of the failed specimen. This is done electrically and failure automatically stops the counter. The machine accommodates ten specimens simultaneously. The principle is shown diagrammatically in Figure 10.

STEEL CORD FATIGUE TESTING

Steel tire cord consists of bundles of finely drawn wires laid together on a rope-making machine. There is a practical limit to the fineness to which a wire may be drawn and this limit is much greater than with a textile fiber. A textile cord, made from rayon yarn of filament denier in common use today, of comparable size to a 21 strand steel cord would have about 2000 filaments. Thus the behavior of a steel cord, as distinct from a textile cord, tends to be influenced more by the properties of the steel from which it is made than by its construction. Table VI gives data on three cords made from wire drawn to different tensile strengths. The increased work hardening, although increasing the tensile strength, decreases the compression fatigue resistance under the conditions of test.

TABLE VI

FATIGUE LIFE OF WIRE CORD MADE FROM WIRE DRAWN TO DIFFERENT TENSILE STRENGTHS. WIRE CONSTRUMCTION: 21 STRANDS OF 0.0058 IN. DIAMETER

Tensile strength of wire, kg./sq. mm.	Breaking strength of cord, lb.	Flexes to break
250	163.9	9900
270	181.4	7510
320	202.9	7350

SUMMARY

The cords in the sidewall of a tire are subject to continual cyclic stresses as the tire is flexed when running. This flexing action leads to a gradual reduction in tensile strength until eventually the cords in the sidewall break. The ability to withstand this continual flexing is termed the fatigue resistance of the cord. The greater the number of flexes before failure of a particular cord, the better the fatigue performance of that cord.

Fatigue resistance of a tire is normally measured by the mileage the tire runs before failure either by running a tire on a test vehicle or on a rotating drum test machine. It is usually found that the drop in tensile strength is greatest in the inner plies of the tire, i.e., in those cords which undergo axial compression rather than tension.

Numerous methods have been proposed for evaluating the fatigue resistance of cords on laboratory machines. They all produce a flexing action on the cord and a drop in tensile strength. Although all of them have been able to detect differences amongst cords, few have revealed a positive correlation with actual tire performance. It seems doubtful, therefore, whether many of the testers actually reproduce the mechanism of fatigue failure in a tire and they may produce results which are misleading. The different types of test which have been published are critically reviewed. Characteristics of tire cord and tire construction which have a bearing on the fatigue resistance of a tire are considered.

It is concluded that fatigue resistance of a cord is influenced by its being molded in a rubber-cord matrix during its flex life and that any successful laboratory fatigue tester must try to reproduce as nearly as possible the mechanism of failure in tire.

A laboratory textile tire cord fatigue tester is described which duplicates cord fatigue characteristics and which causes similar relative strength losses as

are found in tires in service. Using this tester it is shown that cord twist plays an important part in the fatigue life of textile tire cords. The tester has also been used to examine the causes of fatigue in cotton tire cord. It is concluded that the failure is due to fiber damage but the real cause of that damage has not been found. Fatigue in tire cord appears to be somewhat analogous to that in metal in that damage within the structure is much deeper than surface examination would indicate.

Steel tire cord fatigue is rather different from textile cord fatigue and a tester is described for testing this material. It is shown that although work-hardening increases the tensile strength of the wire, the compression fatigue resistance is reduced.

ACKNOWLEDGMENTS

CONFERENCE DISCUSSION

Mr. Whitaker asked whether the author could give any details of the theoretical or actual compression and extension of the inside cord during tests, and also whether he had any further information on the newer fibers, such as Terylene and nylon, as compared with the rayon fibers mentioned in the paper.

Mr. Goy replied that with regard to the first part of the question those details were rather complex and for that reason he had considered them outside the scope of the paper.

In comparing nylon and Terylene with rayon on the fatigue tester, similar difficulties arose as those experienced in tire testing. Adhesion of Terylene to rubber is difficult and the growth of ordinary high tenacity nylon is extremely high. Hence it is extremely difficult to set the same conditions for each cord. In tire building the usual method of overcoming the growth of nylon is to build extra plies into the tire. Hence each cord is stressed at a much lower range than an equivalent rayon tire and one would therefore expect an improved fatigue performance. Evidence suggests that if a rayon and nylon tire were built with equivalent casing strengths in the same size there would be very little difference in the fatigue performance.

Dr. Gardner asked wehther the author had any information on the effect of the dips that were normally employed on the fatigue of various types of cord.

Mr. Goy, in reply, said they did have an effect and it was mentioned in the paper, the question being fully answered in the last paragraph of the introduction.

Dr. Garnder further asked whether it was possible to separate the effect of adhesion fatigue failure from the effect of the dip on the fatigue failure of the cord itself.

Mr. Goy replied that he had not seen any indication of that; excessive depth might lead to that sort of thing.

A Delegate asked whether the author could say a few words about the connection between extensibility and fatigue resistance. There had been a question raised as to the connection between high extensibility and high twist being a relation with high fatigue: was there a second order effect of extensibility?

MR. GOY, in reply, said that there was possibly a connection, although there was evidence from tire testing that a stretched cord had just as good a fatigue resistance as an unstretched cord.   If one got too high a stretch in the cord, in tire testing or with the fatigue tester, it would lead to growth and cracking, which invalidated the test, so within the test there did not seem to be any first order correlation between extensibility and fatigue resistance.   Naturally if one had a high extensibility cord on the outside the compression on the inside would not be so great as with a low extensibility cord on the outside.

MR. FOTHERGILL said that the suggestion was made that strength was the primary criterion in judging fatigue, but personally he doubted it.   If the nature of the fiber itself was changed, even if the construction of the cord was identical in both, the line indicating the loss of strength could fall steeply from a high value or it could fall shallowly from a low value, and the fiber having the lower strength could have the longer fatigue life.   The effect was actually shown in the graph in Figure 4, although there the effect was due to twist, but a difference of that kind could be due to inherent fiber properties.

Turning to Figure 3, a point was shown there, indicating the cord breaking strength when the load on the belt was zero, but he would have thought that the belt would be perfectly circulr and low fatigue would be experienced.   Was it meant to indicate the strength before any fatigue took place?   If that was so, the problem then arose of what exactly was meant by tensile fatigue and compressional fatigue?   It appeared that the author had tried to draw a distinction between the sort of conditions one had in a dynamically balanced fatigue tester, in which the cord was stretched and then caused to oscillate about its stretched length, and the conditions which were met with when the length of the cord tended to be reduced by being bent on the inside of a belt or the inner wall of a tire.   Why did the cords on the outside of the belt behave in exactly the same way as those on the inside when the twsit was varied?   On the B.B. tester increasing twist reduced fatigue life; on the compression type of tester increase of twist increased fatigue life, but on the belt tester described by the author, increasing twist on both inside and outside increased fatigue life.   In other words, although one was supposed to assume that the outer cords were subject to a tensile fatigue they did not behave as cords subjected to a simple tensile test behaved.   In Figure 3 it was indicated that higher loading of the circular belt increased the rate of loss of strength on the inner ply, even though the effect was supposed to be produced by compression, but it seemed that more heavily loading that belt ought to reduce the amount of compression, so that one would have expected it to have a longer life the heavier the load.

MR. GOY, in reply, said with regard to the first point the reference quoted did say "with adequate twist", and presumably that implied that the slope of the curve representing loss of strength would be low.   Hence the higher the starting strength, the longer the life of the particular tire in which the cord was incorporated.

If one tests the cords out of a tire after it has done its useful life, one normally finds a slight drop in strength in the outer plies, which have been operating under tension, with a large drop on the inner plies, which have been under compression.   The lower the twist the greater the drop in strength of both inner and outer plies.   A similar effect is observed with the belt tester described in this paper.   It was not intended to suggest that the cords on the outside of the belt, or the outer plies of a tire for that matter, behaved in the same way was a cord on a dynamically balanced fatigue tester.

The loads employed in the experiment establishing the curve shown in Figure 3 are not very high and would not stretch the belt very much. Higher loads would probably produce the effect of reduction of compression, as suggested, but so far experiments in that direction have only produced looseness and converted the tester into an extremely good dynamic adhesion tester.

A DELEGATE queried one of the author's conclusions, that a degradation of the actual filaments of the cord took place. That finding was contrary to those of one set of authors he had quoted, the paper of Williams, Hannell and Swanson, who had found that although there was a loss in cord strength there was no loss in filament strength. He was himself using the belt fatigue tester, although not the same type as Mr. Goy's, and he agreed with the conclusions of those three authors. In his own testing the cord was rayon and not cotton, and he wondered if that was the difference—if there was evidence of cotton degradation or whether the authors was claiming that one got degradation of the filaments with rayon too?

MR. GOY said the claim was for degradation of cotton fibers only, and it did not necessarily follow that rayon fatigue was the same as cotton. Cord twists had a significant effect on tire cord fatigues: in a rayon cord the twist was put there purely to give a consolidated cord of good fatigue performance, whereas in the cotton cord it was also the means of obtaining the short staple fibers in a continuous yarn length in order to give a continuous cord. Cotton was not a back number as a tire cord, and it was only on economic grounds that rayon was used extensively in the tire trade at the present time. It was still possible to make as good a tire cord from cotton as from rayon.

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ANALYTICAL METHODS FOR CALCULATING TEMPER-
ATURES INSIDE RUBBER ARTICLES DURING
VULCANIZATION *

V. O. Fogel

Heating conditions for the vulcanization of rubber articles have been chosen in a purely experimental way up to the present time. Thus, in one tire plant, research on the question of the most efficient heating conditions for tire vul- canization has consisted of making dozens of experiments on the several vari- ables of heat conductors, and then using the experimental temperature curves for further development.

However, such experiments under industrial conditions not only require considerable time and material, but yield results which inevitably deviate from the true heating conditions in many cases. These deviations are due to fluctu- ations in the steam pressure and water temperature in the course of vulcaniza- tion, nonhomogeneity of material in the group of rubber articles being tested, etc. All these sources of error confuse the results of comparative experiments to a large extent, often making it impossible to reach any general conclusions.

Undoubtedly the most accurate method of determining the ideal heating conditions for vulcanization is a combination of the calculation and experimental methods. In the vulcanization of rubber articles, as in some other branches of industry, heating conditions can be chosen satisfactorily through a preliminary calculation of the temperatures inside the articles, i.e., by a theoretical projec- tion of the heating conditions, followed by a final experimental verification of the calculated results.

The application of calculation methods for determining temperatures in articles during vulcanization is complicated somewhat by the complexity of the analytical solution of equations for the unsteady heating state. However, for the typical heating conditions employed in vulcanization in presses, individual vulcanizers and autoclaves, it is possible to simplify considerably the calculation of temperatures inside articles being vulcanized through the use of curves and tables which we have prepared on the basis of the theory of heat conductivity. This paper concerns the development of methods for such calculations.

All present-day methods for calculating temperatures[1] under unsteady heat- ing conditions fall into two basic groups: analytical and differential calculation methods.

The analytical methods find application for the simplest initial conditions (a constant initial surface temperature of the article, and an initial distribution of temperatures inside the article which is either linear or quadratic), and for the simplest boundary conditions (a constant surface temperature, an increase in surface temperature proportional to time, and a constant heat intensity on the surface).

The advantage of analytical methods is that by using the equations which

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have been developed, in conjunction with the tables and curves given, it is possible to determine rapidly the temperature at any given point in the article at any moment of time during heating or cooling.

In cases where the analytical methods of calculation are inapplicable because of complex boundary conditions, irregular initial temperatures, local heat losses or nonhomogeneity of the article, the temperature calculation may be made by differential methods.

Let us now consider the analytical temperature calculation methods which are applicable to the heating conditions used in the vulcanization of rubber articles. When these are vulcanized in vulcanization presses and individual vulcanizers, the temperature of the mold, which is heated by steam, is deter-
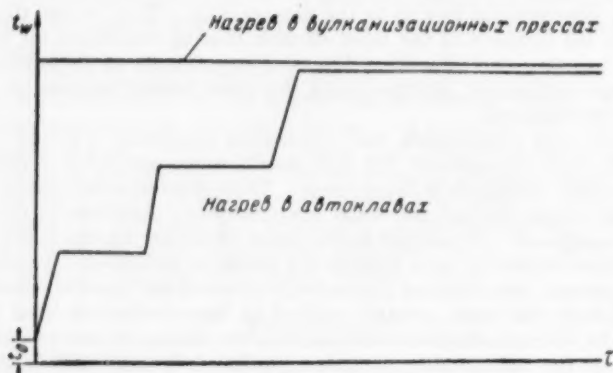
Fig. 1.—Types of heating conditions for vulcanization. The top legend reads, heating in vulcanization presses; the bottom one, heating in autoclaves. The abscissa represents time, the ordinate temperature.

mined by the steam pressure and remains practically constant during the course of vulcanization (Figure 1). Thus in articles vulcanized in such vulcanizers, the temperature of the layers adjacent to the mold surface may be computed by an analytical method, assuming a constant initial temperature inside the articles (t_0 = constant) and a constant surface temperature (t_w = constant).

When articles are vulcanized in autoclaves, however, a stepwise system of heating is usually used (Figure 1). Here the rise in temperature at the surface of the mold may be considered linear with time during certain periods, while during other periods it remains constant.

For articles vulcanized in autoclaves, the temperature on the boundary between the mold and the rubber article can, therefore, be computed analytically from the following assumptions:

(a) for the periods of heating mentioned first, the initial temperature t_0 is constant, while the temperature at the mold surface increases in proportion to time ($t_w = t_0 + b\tau$);

(b) for the remaining heating periods, as we shall see further on, the initial temperature inside the mold changes as a quadratic function ($t_0 = t_w - A\chi + B\chi^2$), while the surface temperature of the mold, t_w, remains constant.

Below are given the equations, tables and curves for temperature calculation under these three types of heating conditions, which are applicable to an article

with the simplest possible shape, namely, a homogeneous flat slab heated uniformly on both sides, with a thickness which is much less than its length or width.

In the subsequent sections of this paper this method is extended to apply to composite (plied up) slabs, cylindrical segments and rectangular blocks.
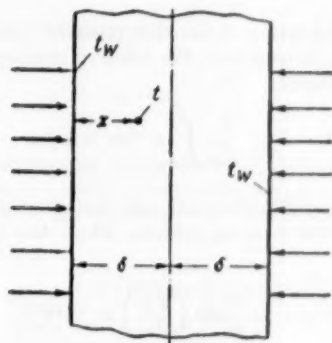
FIG. 2.—Heating of an infinitely wide flat slab.   (Note: the symbols are described in the text.)

Let us use the following designations (Figure 2):

δ is the maximum length of the line of heat flow (for a flat slab, one-half of its thickness;

χ is the distance from the heated surface to the point whose temperature is to be determined;

$a = \lambda/C\gamma$ is the thermal diffusivity of the material of which the slab is composed, which depends on its thermal conductivity λ, its specific heat C and its specific gravity γ;

τ is the period of heating;

t_0 is the initial internal temperature of the slab;

t_w is the surface temperature of the slab;

t_c is the temperature at the center of the slab;

t is the temperature of the given point;

$F_o = a\tau/\delta^2$ is the Fourier number characterizing unsteady-state heating conditions;

$z = \chi/2\sqrt{a\tau}$ is the space-time coordinate of a point in a semi-infinite body $(\delta \to \infty)$; and

$$\theta = \frac{t - t_0}{t_w - t_0} \quad \text{and} \quad \theta_c = \frac{t - t_c}{t_w - t_c}$$

are the relative temperature increases.

From the theory of thermal conductivity for unsteady heating processes[2] we have derived the equations for the temperature field in the three sets of heating conditions in which we are interested:

1. When the initial internal temperature t_0 of the slab and its surface temperature t_w are both constant, the relative temperature increase equals:

$$\theta = 1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1} \sin \left[(2n - 1) \frac{\pi}{2} \frac{\chi}{\delta} \right]}{2n - 1} e^{-\left[(2n - 1) \frac{\pi}{2} \right]^2 F_0} \tag{1}$$

When $F_0 < 0.05$, the heating of the slab proceeds just as in a semi-infinite body, in which, where t_w is constant, the relative temperature increase equals one plus Gauss' error integral:

$$\theta = 1 - \frac{2}{\sqrt{\pi}} \int_0^z e^{-z^2} dz = erfcz \tag{1a}$$

When $F_0 > 0.25$, it is sufficient to use only the first term of the series in (1); here we approach a regular heating system, where the temperature increases exponentially with time:

$$\theta = 1 - \frac{4}{\pi} \sin \left(\frac{\pi}{2} \frac{\chi}{\delta} \right) e^{-(\pi^2/4)F_0} \tag{1b}$$

Where $F_0 \geqslant 2.9$, $\theta = 1$ with an accuracy of 0.001. $\hspace{2cm}$ (1c)

2. When the initial internal temperature t_0 of the slab is constant, and its surface temperature increases proportionally to time ($t_w = t_0 + b\tau$), then

$$\theta = 1 - \frac{\frac{\chi}{\delta} \left(2 - \frac{\chi}{\delta} \right)}{2F_0}$$

$$+ \frac{16}{\pi^3 \cdot F_0} \sum_{n=1}^{\infty} \frac{(-1)^{n+1} \sin \left[(2n - 1) \frac{\pi}{2} \frac{\chi}{\delta} \right]}{(2n - 1)^3} e^{-\left[(2n - 1) \frac{\pi}{2} \right]^2 F_0} \tag{2}$$

When $F_0 < 0.05$, the heating of the slab is like that of a semi-infinite body, for which, where the surface temperature increases proportionally to time, we have derived the following equation:

$$\theta = (1 + 2z^2)erfcz = \frac{2z}{\sqrt{\pi}} e^{-z^2}$$

When $F_0 \geqslant 0.25$ we may use only the first term of Equation (2):

$$\theta = 1 - \frac{\frac{\chi}{\delta} \left(2 - \frac{\chi}{\delta} \right)}{2F_0} + \frac{16}{\pi^3 F_0} \sin \left(\frac{\pi}{2} \frac{\chi}{\delta} \right) e^{-(\pi^2/4)F_0} \tag{2b}$$

but when $F_0 > 2.2$, the following is accurate within 0.001:

$$\theta = 1 - \frac{\frac{\chi}{\delta} \left(2 - \frac{\chi}{\delta} \right)}{2F_0} \tag{2c}$$

By the use of Equation (2c) it is easy to show that when the surface temperature of the slab increases proportionally to time ($t_w = t_0 + b\tau$) and $F_0 > 2.2$, the temperature inside the slab changes according to a parabolic equation:

$$t = t_w - \frac{b}{2a} \chi (2\delta - \chi)$$ (2d)

whereas in the center of the slab

$$t_c = t_w - \frac{b\delta^2}{2a}$$ (2e)

3. When the initial internal temperature of the slab changes quadratically (Equation (2d)) while the surface temperature t_w and the initial temperature in the center of the slab t_c are constant, then the relative temperature increase equals

$$\theta_c = \frac{t - t_c}{t_w - t_c} = 1 - \frac{32}{\pi^3} \sum_{n=1}^{\infty} \frac{(-1)^{n+1} \sin\left[(2n - 1) \dfrac{\pi}{2} \dfrac{\chi}{\delta}\right]}{(2n - 1)^3} e^{\left[(2n - 1) \frac{\pi}{2}\right]^2 F_0}$$ (3)

When $F_0 > 0.2$, we may limit ourselves to the first term in Equation (3):

$$\theta = 1 - \frac{32}{\pi^3} \sin\left(\frac{\pi}{2} \frac{\chi}{\delta}\right) e^{-(\pi^2/4)F_0}.$$ (3a)

When $F_0 \geqslant 2.9$, then with an accuracy of 0.001, $\theta_c = 1$.

When we compare Equations (1), (2) and (3), we see that for any given relation $t_w = f(\tau)$, they can all be expressed by an equation of the type

$$\theta = F\left(F_0, \frac{\chi}{\delta}\right)$$ (4)

That is, the relative temperature increase in a homogeneously heated slab depends only on the Fourier number and the relative coordinates of the given point.

When the values of the Fourier number are low ($F_0 < 0.05$), the heat flow warms up only the layer of the slab which is adjacent to the heating surface, and therefore the heating of the slab conforms to the rule for the heating of a semi-infinite body:

$$\theta = F(z)$$ (5)

Table I and Figures 3, 4, 5 and 6 show the calculated values for the relative temperature increases in the three main types of vulcanization heating systems we have considered. The following example will suffice to show the method by which the tables and curves mentioned above are employed.

In the course of a vulcanization, the temperature of the outer surface of a steel mold 35 mm. thick rose linearly from $t_0 = 90°$ C to $t_w = 130°$ in a period of 4 minutes, and then remained constant at $t_w = 130°$ for another 4 minutes;
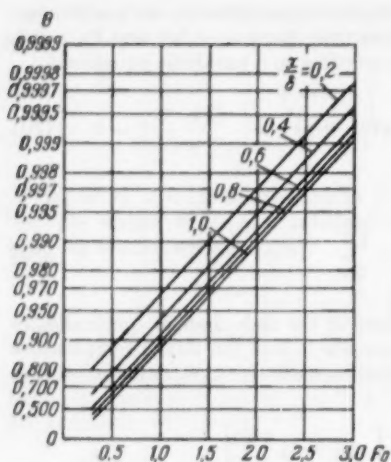
FIG. 3.—Relative temperature increases in a
flat slab where the initial and surface tempera-
tures t_0 and t_w are constant. The abscissa rep-
resents the Fourier number, the ordinate the
temperature increase θ.
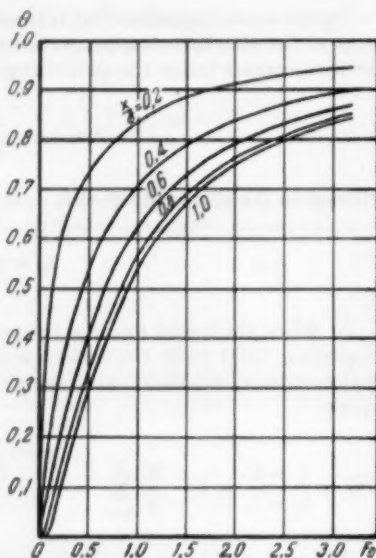
FIG. 4.—Relative temperature increases in a
flat slab where the initial temperature t_0 is con-
stant and the surface temperature t_w increases
proportionally to time $(t_w = t_0 + b\tau)$. The
abscissa represents the Fourier number, the
ordinate the temperature increase θ.
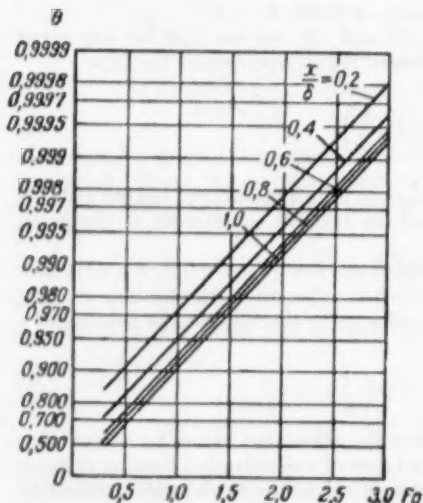
FIG. 5.—Relative temperature increases in a flat slab
where the initial internal temperature of the slab changes
quadratically $(t_0 = t_w - Ax + Bx^2)$ and the surface
temperature t_w is constant. The abscissa represents
the Fourier number, the ordinate the temperature
increase θ.
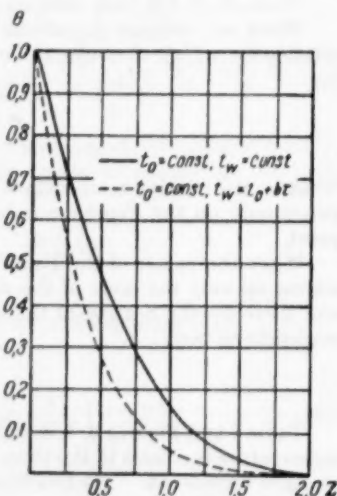
FIG. 6.—Relative temperature increase in
a semi-infinite body. The abscissa repre-
sents the space-time coordinate z, the or-
dinate the relative temperature increase θ.

it is required to determine the temperature on the boundary between the mold and the rubber article being vulcanized after 4, 6 and 8 minutes of vulcanization.

The thermal diffusivity of steel,

$$a = \frac{\lambda}{c\gamma} = \frac{39}{0.11 \times 7900} = 45 \times 10^{-3} \text{ sq. meter per hour}$$

is 70–90 times that of rubber. Hence we must consider the heating conditions in a steel mold as being equivalent to those in a slab heated only one on side, on the assumption that the temperature gradient on the inner surface of the mold is zero. (In actual practice, accurate calculations have shown it to be less than $0.1°$ C per mm.)

TABLE I

DEPENDENCE OF THE RELATIVE TEMPERATURE INCREASE θ IN A SEMIINFINITE BODY AND IN SLABS WHERE $F_0 < 0.05$, ON THE SPACE–TIME COORDINATE z UNDER TYPICAL VULCANIZATION HEATING CONDITIONS

$z = \chi/2\sqrt{a\tau}$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$t_0 = $ constant $t_w = $ constant	1	0.887	0.777	0.671	0.572	0.479	0.396	0.322	0.258	0.203
$t_0 = $ constant $t_w = t_0 + b\tau$	1	0.794	0.622	0.483	0.370	0.280	0.210	0.154	0.113	0.081
z	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9
$t_0 = $ constant $t_w = $ constant	0.157	0.120	0.090	0.066	0.048	0.034	0.024	0.016	0.011	0.007
$t_0 = $ constant $t_w = t_0 + b\tau$	0.057	0.040	0.027	0.018	0.012	0.009	0.006	0.003	0.002	0.001
z	2.0	2.1	2.2	2.3	2.4	2.5				
$t_0 = $ constant $t_w = $ constant	0.005	0.003	0.002	0.001	0.001	0				
$t_0 = $ constant $t_w = t_0 + b\tau$	0.001	0	0	0	0	0				

At the end of the first period of the heating of the mold ($\tau = 4$ minutes $= 1/15$ hour), the Fourier number equals

$$F_0 = \frac{a\tau}{\delta^2} = \frac{45 \times 10^{-3}}{15 \times 0.035^2} = 2.45$$

From Figure 4 we find the relative temperature increase for this value of F_0 where $\chi = \delta$, for the case where the temperature of the outer surface of the mold increases linearly:

$$\theta = \frac{t - t_0}{t_w - t_0} = \frac{t - 90}{130 - 90} = 0.796$$

whence the temperature of the inner surface of the mold at the end of this period equals:

$$t = 90 + 0.796 \, (130 - 90) = 121.8° \text{ C}$$

For the second period of heating, when t_w is constant and equals 130° C, t_c = 121.8°. After the next two minutes of heating, when t_w is constant, F_0 = 1.22. From Figure 5 we find that when $\chi = \delta$:

$$\theta_c = \frac{t - t_c}{t_w - t_c} = \frac{t - 121.8}{130 - 121.8} = 0.950$$

Hence the temperature on the inner surface of the mold 6 minutes after the start of the heating equals

$$t = 121.8 + 0.950(130 - 121.8) = 129.6° \text{ C}$$

During the last 2 minutes of heating, when t_w is constant, $F_0 = 2.45$. From Figure 5, we find that when $\chi = \delta$

$$\theta_c = \frac{t - t_c}{t_w - t_c} = \frac{t - 121.8}{130 - 121.8} = 0.998$$

Whence the temperature of the inner surface of the mold 8 minutes after the start of heating equals

$$t = 121.8 + 0.998(130 - 121.8) = 130° \text{ C}$$

The example given above shows that when the temperature at the surface of the mold increases linearly, the relative drop in temperature inside it is quite considerable and cannot be ignored. However when the heating is stepwise and t_w is kept constant, the temperatures inside the mold quickly become equalized.

Vulcanized rubber articles are not always homogeneous in composition throughout. In many cases they may be considered as separate slabs closely joined together, each of which has its characteristic thermophysical constants. Thus the experimental data of Frumkin and Dubinker[3] show that in a tire the thermal diffusivity of the breaker is about 15 per cent lower than that of the tread, while that of the carcass is 20 per cent lower.

At the points of contact between the component plies of such a layered slab, the temperatures should be equal, and the ratio of their temperature gradients should be inversely proportional to the ratio between their respective coefficients of thermal conductivity. Hence any accurate equations for calculating the temperatures inside the component plies are necessarily rather complex[4].

However, by the use of Equation (4) we may propose the following approximate method for calculating temperatures in such a layered slab, where the outer layer of stock contiguous to the heating surface is somewhat thicker than any of the other layers, and where the thermophysical constants of these separate component parts of the slab differ only slightly.

As was noted above, for a given relation $t_w = f(\tau)$, the Fourier number and the relative coordinate of the point in question are the basic determining factors in the calculation of the relative temperature increases.

Thus the required condition for an equalized temperature field throughout a layered slab is that the Fourier numbers of its separate component parts must be equal:

$$F_{o_1} = F_{o_2} = F_{o_3} = \cdots = F_{o_n}$$

or

$$\frac{a_1 \tau_1}{\delta_1^2} = \frac{a_2 \tau_2}{\delta_2^2} = \frac{a_3 \tau_3}{\delta_3^2} = \cdots = \frac{a_n \tau_n}{\delta_n^2} \tag{6}$$

where a_n and δ_n are the thermal diffusivity and thickness, respectively, of a component layer of the nonhomogeneous slab.

It is necessary that we determine the relative temperature increase for exactly the same period of time in each case; hence $\tau_1 = \tau_2 = \tau_3 = \cdots = \tau_n$. Then from Equation (6) we may derive this proportion:

$$\frac{a_1}{\delta_1^2} = \frac{a_2}{\delta_2^2} = \frac{a_3}{\delta_3^2} = \cdots = \frac{a_n}{\delta_n^2}$$

or

$$\frac{a_1}{\delta_1^2} = \frac{a_1}{\left(\sqrt{\dfrac{a_1}{a_2}}\,\delta_2\right)^2} = \frac{a_1}{\left(\sqrt{\dfrac{a_1}{a_3}}\,\delta_3\right)^2} = \cdots = \frac{a_1}{\left(\sqrt{\dfrac{a_1}{a_n}}\,\delta_n\right)^2}$$

This last expression may be converted into the following:

$$\frac{a_1}{\delta_1^2} = \frac{a_1}{\delta^2_{2\text{equiv.}}} = \frac{a_1}{\delta^2_{3\text{equiv.}}} = \cdots = \frac{a_1}{\delta^2_{n\text{equiv.}}}$$

where

$$\delta_{n\text{equiv.}} = \sqrt{\frac{a_1}{a_n}} + \delta_n \tag{7}$$

From the form of Equation (7) we may draw the following conclusion: in calculating the temperatures inside a salb of nonhomogeneous composition, we may theoretically substitute for this slab an equivalent homogeneous slab with a thermal diffusivity equal to that of any one of the component layers (e.g., a), provided that we substitute an equivalent thickness of each layer of the slab, calculated from Equation (7), for its actual thickness.

The relative coordinate of the point, χ/δ, can be replaced by a corresponding quantity $\chi_{\text{equiv.}}/\Sigma\delta_{\text{equiv.}}$, the Fourier number for the equivalent slab being:

$$F_o = \frac{a_1 \tau}{(\Sigma\delta_{\text{equiv.}})^2}$$

Through such a substitution we may calculate temperatures in a slab of nonhomogeneous composition. An example of such a calculation is found in the concluding section of this paper.

In many cases the rubber articles whose internal temperatures must be calculated are not flat but rather in the form of hollow cylinderical segments heated from both the inside and the outside. As Figure 7 shows, in the outer surface layers of such segments, the lines of heat flow converge radially, and consequently these layers are heated more intensely than in a flat slab. In
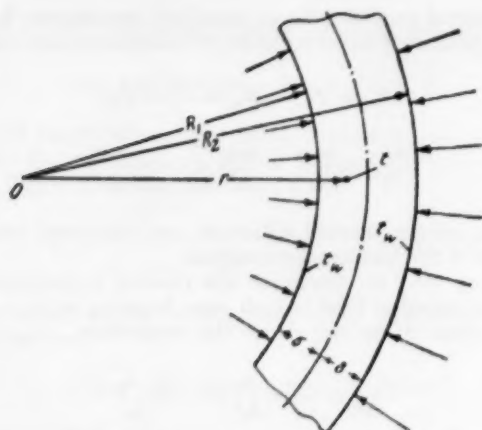
FIG. 7.—The heating of a hollow cylindrical segment.

the inner surface layers of cylindrical segments, however, the lines of heat flow diverge, and these layers are heated less intensely than in a flat slab.

If we use the designation $\Delta t_{slab} = t_w - t$ for a flat slab and $\Delta t_{cyl.} = t_w - t$ for a cylindrical segment, then the above-mentioned relation between the change in intensity of heating in cylindrical segments and that in flat slabs may be represented by the coefficient $\varphi = \Delta t_{cyl.}/\Delta t_{slab}$. For the outer surface layers of cylindrical segments this coefficient is less than unity; for the inner ones, greater than unity.

In order to estimate the value of the coefficient φ, a number of calculations were made of the relative drops in temperature in cylindrical segments and flat slabs having the same thermal diffusivity and thickness, where the surface temperatures increased linearly. Under these conditions, and with $F_0 > 2.2$,

$$\varphi = \frac{\Delta t_{cyl.}}{\Delta t_{slab}} = \frac{R_2{}^2 \ln \frac{r}{R_1} + R_1{}^2 \ln \frac{R_2}{r} - r^2 \ln \frac{R_2}{R_1}}{\chi(2\delta - \chi) \ln \frac{R_2}{R_1}} \tag{8}$$

TABLE II

VALUES OF THE COEFFICIENT $\varphi \dfrac{\Delta t_{CYL.}}{\Delta t_{SLAB}}$ AS RELATED TO THE RELATIVE COORDINATE OF THE POINT IN QUESTION AND THE RATIO BETWEEN THE OUTER AND INNER RADII OF THE CYLINDRICAL SEGMENT (WHERE $F_0 > 2.2$)

	R_2/R_1									
	Outer layer					Inner layer				
χ/δ	1.1	1.2	1.3	1.4	1.5	1.1	1.2	1.3	1.4	1.5
0.1	0.988	0.978	0.970	0.963	0.955	1.013	1.026	1.040	1.053	1.065
0.2	0.991	0.983	0.978	0.973	0.966	1.010	1.021	1.031	1.041	1.048
0.3	0.994	0.989	0.985	0.981	0.978	1.007	1.013	1.019	1.025	1.032
0.4	0.997	0.995	0.993	0.992	0.990	1.003	1.007	1.010	1.014	1.017
0.5	1.000	1.001	1.002	1.003	1.003	1.000	1.001	1.002	1.003	1.003

where R_1 and R_2 are the inner and outer radii of the cylindrical segment; r is the distance between the given point and the center of the cylinder; χ is the distance between the given point and the heating surface (for the outer surface layers $\chi = R_2 - r$, for the inner ones $\chi = r - R_1$); and $2\delta = R_2 - R_1$ is the thickness of the cylindrical segment and the flat slab.

The results of the calculations with Equation (8) were obtained with the aid of the common logarithms of various values of the ratios R_2/R_1 and χ/δ, given in Table II.

As the data in Table II show, when the ratio between the outer and inner radii of the cylindrical segment, R_2/R_1, is less than 1.5, the center layer of the

TABLE III

VALUES OF THE COEFFICIENT $\psi = \Delta t_{BLOCK}/\Delta t_{SLAB}$ AS RELATED TO THE RELATIVE COORDINATES χ/δ_1 AND y/δ_2 OF POINTS AND TO THE RATIO BETWEEN THE SIDES OF THE RECTANGULAR BLOCK (WHERE F_0 2.2)

| | $\delta_2/\delta_1 = 1$ | | | | | $\delta_2/\delta_1 = 2$ | | | | |
| | y/δ_2 | | | | | y/δ_2 | | | | |
χ/δ_1	0.0	0.2	0.4	0.6	.08	0.0	0.2	0.4	0.06	0.8
0.0	0.588	0.569	0.506	0.396	0.232	0.909	0.892	0.828	0.684	0.451
0.2	0.593	0.577	0.512	0.403	0.233	0.914	0.897	0.831	0.689	0.452
0.4	0.605	0.586	0.520	0.411	0.245	0.914	0.900	0.836	0.701	0.465
0.6	0.619	0.604	0.539	0.427	0.262	0.914	0.903	0.846	0.711	0.481
0.8	0.644	0.621	0.572	0.466	0.292	0.922	0.903	0.852	0.735	0.502

| | $\delta_2/\delta_1 = 3$ | | | | | $\delta_2/\delta_1 = 5$ | | | | |
| | y/δ_2 | | | | | y/δ_2 | | | | |
χ/δ_1	0.0	0.2	0.4	0.6	0.8	0.0	0.2	0.4	0.6	.08
0.0	0.978	0.973	0.938	0.837	0.600	1.000	0.995	0.990	0.955	0.789
0.2	0.980	0.975	0.941	0.842	0.602	1.000	0.995	0.990	0.956	0.788
0.4	0.980	0.975	0.941	0.845	0.612	0.998	0.995	0.990	0.958	0.791
0.6	0.980	0.976	0.946	0.850	0.625	1.000	0.997	0.990	0.960	0.796
0.8	0.981	0.978	0.978	0.862	0.652	1.000	0.997	0.992	0.964	0.814

| | $\delta_2/\delta_1 = 10$ | | | | |
| | y/δ_2 | | | | |
χ/δ_1	0.0	0.2	0.4	0.6	0.8
0.0	1.000	0.996	0.996	0.995	0.958
0.2	1.000	0.997	0.997	0.997	0.958
0.4	1.000	0.998	0.997	0.997	0.958
0.6	1.000	1.000	0.997	0.997	0.958
0.8	1.000	1.000	0.997	0.997	0.966

segment receives practically the same intensity of heating as the center layer of the slab. At the same time, the heating of the outer surface layer is 1–5 per cent more intense than at the corresponding outer layer of a flat slab, while that of the inner layer is 1–6 per cent less intense than in the slab. All of the above presumes a linear increase in the surface temperature and a value of $F_0 > 2.2$.

With lower values of the Fourier number and a constant temperature at the surface of the cylindrical segment, as Figures 3, 4 and 5 show, the equalization of temperatures inside the articles is more rapid than with a linear increase in the surface temperature; and in this case the temperature fields in cylindrical segments where $R_2/R_1 \leq 1.5$ and those in flat slabs differ from one another still less, so that the calculation of Δt for cylindrical segments where $R_2/R_1 \leq 1.5$ may be made with the same tables and curves used for flat slabs.

In the previous paragraphs we have considered the calculation of temperatures in one-dimensionally heated bodies—flat slabs and cylindrical segments. However in some cases it is impossible to ignore the heat supplied through the lateral surfaces of the body, and we must then calculate temperatures in bodies heated two- and three-dimensionally.

In order to reveal the effect of the heat supplied through lateral surfaces on the temperature field in a finite slab, relative temperature calculations were made for rectangular blocks with a surface temperature increasing linearly and a value of $F_0 > 2.2$.

The ratios between the sides of the rectangular blocks, δ_2/δ_1, employed in this study were 1, 2, 3, 5 and 10. The calculations showed that when the ratio δ_2/δ_1 between the sides is greater than 5, the center of the block is heated with the same degree of intensity as in an infinite flat slab. Only when the value of δ_2/δ_1 is less than 5 is it necessary to introduce the appropriate corrections.
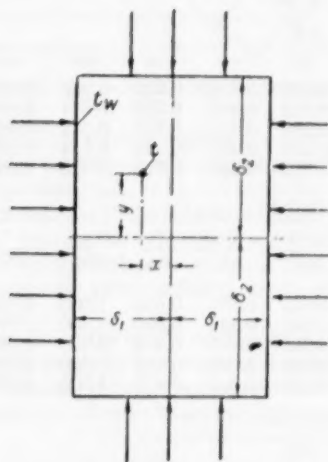
FIG. 8.—The heating of a rectangular block.

In order to evaluate the effect of the heat supplied through the side surfaces of a block on its temperature field, we have prepared Table III in which values of the coefficient $\psi = \Delta t_{block}/\Delta t_{slab}$ are given for $F_0 = a\tau/\delta_1^2 > 2.2$, where $\Delta t_{block} = t_w - t$ for a rectangular block and $\Delta t_{slab} = t_w - t$ for a slab with a thickness of $2\delta_1$.

The center of symmetry of the cross-section of the block was taken as the center of the coordinates (Figure 8).

In order to compare the temperatures in articles during vulcanization, as calculated by the method proposed above, with actual experimental data, we carried out a calculation of the temperature field in the outer surface layers of a 9.00–20 automobile tire during its vulcanization in an individual vulcanizer.

The initial temperature t_0 was taken as 32° C, according to the experimental conditions, and the pressure p of the steam for heating as 5.6 kg. per sq. cm., which corresponds to $t_w = 156°$ C.

The thickness of the tread $\delta_1 = 16.0$ mm., the thickness of the breaker

$\delta_2 = 3.4$ mm., and the thickness of the four carcass plies (plies 7–10), heated through the side of the mold, was $\delta_3 = 5.9$ mm.

For the thermophysical characteristics of the rubber, we may adopt the data of Frumkin and Dubinker[3], as corrected by us:

for the tread—$a_1 = 7.1 \times 10^{-4}$ sq. meter per hour;
for the breaker—$a_2 = 6.0 \times 10^{-4}$ sq. meter per hour;
for the carcass—$a_3 = 5.7 \times 10^{-4}$ sq. meter per hour.

TABLE IV

CALCULATED AND EXPERIMENTAL DATA FOR A 9.00-20 TIRE

| | | τ (min.) | | | | | | | |
	$F_o = a\tau/\delta^2$	10 0.171	20 0.342	30 0.514	40 0.685	50 0.856	60 1.027	70 1.199	80 1.370
Point 1 between tread and breaker	θ_1	0.320	0.615	0.747	0.834	0.891	0.929	0.953	0.969
	$t_{calcd.}$	72°	108°	125°	135°	143°	148°	150°	152°
	$t_{expt.1}$	63°	100°	120°	134°	142°	148°	150°	152°
	Per cent deviation	+14.3	+8.0	+4.2	+0.7	+0.7	0	0	0
Point 2 between breaker and carcass	θ_2	0.230	0.505	0.675	0.787	0.860	0.908	0.940	0.961
	$t_{calcd.}$	61°	95°	116°	130°	139°	145°	149°	151°
	$t_{expt.1}$	58°	95°	116°	130°	139°	146°	148.5°	151°
	Per cent deviation	+5.2	0	0	0	0	−0.7	+0.3	0
Point 3 between the 6th and 7th carcass plies	θ_2	0.164	0.452	0.641	0.765	0.846	0.899	0.934	0.956
	$t_{calcd.}$	52°	88°	112°	127°	137°	143°	148°	150°
	$t_{expt.1}$	52°	89°	113°	128°	136°	144°	147°	150°
	Per cent deviation	0	−1.1	−0.9	−0.8	+0.7	−0.7	+0.7	0

Then from Equation (7) the equivalent thicknesses of the breaker and four carcass plies equals

$$\delta_{2\ equiv.} = \sqrt{\frac{7.1}{6.0}} \times 3.4 = 3.7 \text{ mm.}$$

$$\delta_{3\ equiv.} = \sqrt{\frac{7.1}{5.7}} \times 5.9 = 6.6 \text{ mm.}$$

and the sum of the equivalent thicknesses of the outer layers of a tire heated through the side of the mold equals

$$\delta = \Sigma\delta_{equiv.} = 16.0 + 3.7 + 6.6 = 26.3 \text{ mm.}$$

The relative coordinates of the points whose temperatures are to be determined are:

between tread and breaker—$\chi_1/\delta = 16.0/26.3 = 0.608$;
between breaker and carcass—$\chi_2/\delta = 19.7/26.3 = 0.749$;
between the sixth and seventh carcass plies—$\chi_3/\delta = 26.3/26.3 = 1.000$.

The influence of the curvature of the outer layers of the tire was disregarded, since for these $R_2/R_1 < 1.2$.

From this data and by the use of Equations (1) and (1b) we calculated the temperatures given in Table IV and shown graphically in Figure 9 for the three given points in the tire.

These curves also show the experimental points obtained from direct temperature measurements made during the vulcanization of this tire in a certain tire factory.

From the data in Table IV we may conclude that the results of temperature calculation agree satisfactorily with the temperatures as determined experimentally, in the given tire. The only substantial deviation is that noted in the initial period of vulcanization, in those plies of the tire which are adjacent
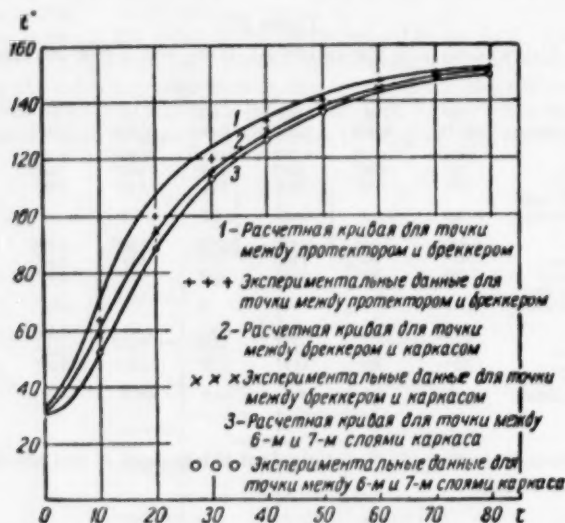
Fig. 9.—Curves of calculated and experimental temperature data for a 9.00-20 tire. *1.* Curve of calculated temperatures for a point between the tread and the breaker. +++, Experimental data for this point. *2.* Curve of calculated temperatures for a point between the breaker and carcass. ×××, Experimental data for this point. *3.* Curve of calculated temperatures for a point between the sixth and seventh carcass plies. 000, Experimental data for this point. The abscissa represents the time τ in minutes, the ordinate the temperature t in ° C.

to the heating surface. This is explained by a drop of 10–15° C in the mold temperature at the start of the vulcanization, relative to the temperature used in the calculation, $t_w = 156°$ C = constant.

However this phenomenon, as Table IV and Figure 9 show, is not reflected substantially in the temperature curves in the later periods of vulcanization, where the experimental points agree with the calculated temperatures with an accuracy of 1° C.

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INFRARED SPECTROSCOPIC ANALYSIS
OF ELASTOMERS *

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INTRODUCTION

The rapidly increasing range of elastomers and polymers used in the rubber industry raises the difficult problem of their analysis. Chemical tests which are relatively specific (e.g., for polyisoprene and polystyrene) need the application of a number of separate tests to each sample. Those which are not specific (e.g., elemental nitrogen for polynitriles, chlorine for polychloroprenes) become less discriminating as the number of possible polymers increases. Refractive index or density measurements may be convenient for synthetic rubber plants, where gum stocks of known origin are involved, but the chemist presented with a sample of unknown origin can seldom profit from such single parameter methods.

What is required in such cases is a method of analysis which is:

(a) applicable to all polymers, copolymers, and mixtures;
(b) independent of molecular weight, state of cure, oxidation, and the like;
(c) unaffected by other compounding ingredients;
(d) applicable on a semimicro or micro scale.

Criterion (a) is satisfied only by a multiparameter technique. Of those at present available infrared absorption spectroscopy best satisfies the other criteria, and has been most widely used for the analysis of polymers. Ultraviolet spectroscopy is a valuable supplementary technique in certain cases but suffers from the disadvantages that it—

(a) is mainly applicable to conjugated systems (in the usual spectral range);
(b) is very sensitive to other compounding ingredients;
(c) normally requires clear solutions. If accurate thickness measurements of very thin films were possible, its applicability might be extended.

While infrared spectroscopy is completely general in the sense that all polymers have spectra which are more or less distinctive, it is necessary to obtain a sample in suitable form for examination. This will be discussed more fully later, but the main difficulty lies in the examination of cured, black-loaded stocks. In order to deal with such intractable cases, combinations of pyrolysis and spectroscopy may be used[1b]. The methods are very simple and quick but have certain limitations; these may be overcome by developing more repeatable conditions of pyrolysis and of the collection of pyrolysates. At present they are regarded in these laboratories mainly as techniques which are supplementary

to direct examination.   An alternative instrumental approach for the examination of black-loaded stocks is under development and is described later.

Infrared spectroscopy is used not only for identification of polymers, but also for their quantitative estimation.   Although considerable development is often necessary to establish procedures for accurate quantitative analyses, it is usually possible to estimate compositions semiquantitatively to within about 5 per cent without appreciable development work; in many cases this is sufficient.

Although the emphasis of this paper is on elastomers, it is not often possible to discriminate between repeating units used in elastomeric and in nonelastomeric polymers.   While as wide a range of materials has been covered as was practical, the selection inevitably reflects to a certain extent the problems and materials encountered in this laboratory.

BASIS OF INFRARED SPECTROSCOPIC METHODS

All organic molecules absorb infrared radiation at specific frequencies which are those of atomic vibrations of the molecules.   The intensity of an absorption is related to the change of dipole associated with the vibration; in general polar and unsymmetrical groups absorb more strongly.   Although the vibrations are those of the molecule as a whole, many bonds and atomic groups give rise to characteristic absorptions which are relatively independent of changes in the rest of the molecule.   A number of charts correlating absorptions with atomic groups have been published[2,3,4] and are of great value in structure diagnosis and analysis.   It is, however, essential to realize that changes in environment may cause appreciable changes of both frequency and absorptivity and such charts should be regarded as guides only.

Frequencies are usually expressed in wave numbers (cm.$^{-1}$) although wavelengths in microns (μ) are sometimes used.   The most convenient unit of intensity for analytical purposes is absorbance, $A = \log I_0/I$ (where I_0 is the incident and I the transmitted energy).   Beer's Law states that $A = abc$ where a is the specific absorptivity, b the optical path length, and c the concentration. In the absence of association or molecular interactions the relationship usually holds, although small deviations are frequently encountered owing to instrumental limitations; it is always advisable to check for Beer's Law in quantitative analyses.

Spectra of polymers.—The spectrum of a low molecular weight compound is that of the individual molecules, and even small changes of structure or configuration cause differences in the spectrum.   However, in a polymer, individual molecules in general have different molecular weights, configurations, branching, and arrangements of repeating units.   The spectrum is therefore that of a large number of slightly different molecules and consequently only those features common to appreciable numbers of the individual molecules are observed.   Polymer spectra, therefore, mainly consist of characteristic absorptions associated with the basic repeating units; in general they are simpler than the spectra of the corresponding monomers, and are little affected by molecular weight[5] or crosslinking[6].   (See, however, chlorosulfonated polyethylene[7] under Sulfones, below.)

Although some interaction between neighboring repeating units must occur, most of the elastomeric copolymers have spectra which are substantially like those of a mixture of the corresponding homopolymers (see, however, copolymers of butadiene and acrylonitrile under Polydienes); this simplifies analyses but is a limitation of the method.

Normally the arrangement of repeating units in a copolymer is random, but there is considerable interest at present in the field of block and graft copolymers in which chains of one repeating unit are linked to chains of another repeating unit. Examples are polyester/urethans and natural rubber/methyl methacrylate graft copolymers (Figure 8). Such copolymers will have spectra which are even more similar to those of mixtures of homopolymers than random copolymers. It is unlikely that infrared methods could distinguish between block polymers, copolymers, and mixtures, except in rare cases.

In general the most characteristic absorptions of hydrocarbon polymer repeating units are those of pendant groups; the saturated skeleton of vinyl polymers is not spectroscopically distinctive, as it gives mainly C—H stretching (ν(CH)) and C—H bending (δ(CH)) vibrations which are common to most aliphatic compounds.

Crystallinity sometimes gives rise to spectral changes, e.g., polychloroprene[8], gutta[9,10], natural rubber[9,10], and polyester/urethans[11] and these differences, when recognized, may be used to help identify these polymers.

EXPERIMENTAL TECHNIQUES

Preparation of samples.—Although for accurate quantitative analyses of gum stocks, samples are usually examined in solutions in suitable solvents (e.g., carbon tetrachloride, carbon disulfide, chloroform), for general work the materials must be in the form of thin uniform films of 0.0005 to 0.005 cm. thickness. This corresponds to 0.4–4 mg. of material (using a film 1.5 × 0.5 cm. in area, with a normal spectrometer; with a microspectrometer[12,13] it could be reduced to about 10 μg.). The size of sample required for analysis is determined by the problem of handling, and varies from a few mg. for uncured materials to about 0.2 g. of cured, black-loaded stock.

The most general method available is to cut thin sections with a microtome (using a freezing stage and suitable lubricant in most cases) and either spread them on rock-salt plates or silver chloride sheets, or hold them in a suitable clamp. Extraction with alcohol or acetone to remove soluble compounding ingredients may be carried out before or after sectioning, and the film must be freed from solvents, preferably in a vacuum oven. The extract may be used for identification of oils and plasticizers (by infrared), or antioxidants and accelerators (by ultraviolet spectroscopy[14]); ultraviolet is more sensitive than infrared[15] to the latter compounds. It is advisable to carry out the extraction quantitatively, as this enables oil-extended or heavily plasticized elastomers to be identified. Insoluble nonpolymeric materials which may give absorptions which are liable to interfere include titanium dioxide (strong absorption from 810 to the sodium chloride cut-off at 650 cm.$^{-1}$), silica (strong absorptions at 1100 to 800 cm.$^{-1}$), clays (strong absorption at 1040 cm.$^{-1}$), and zinc oxide/stearic acid mixtures which give[6] zinc stearate (a sharp band at 1535 cm.$^{-1}$).

Microtomed sections of cured materials containing fillers or carbon black usually have very poor transmissions due to scatter of the energy by the particles of filler or of black. The mean transmission is often as low as 1 per cent and the spectrum cannot be recorded with conventional equipment.

A method which is being investigated in these laboratories is the use of a reflecting microscope of large numerical aperture[12] which collects a larger proportion of the scattered transmitted energy. Preliminary work carried out at King's College, London University, suggests that about ten times as much energy is collected by this method, and it is anticipated that it will be of general

applicability to black-loaded stocks. The spectrum of a GR-S/natural rubber mix containing 60 parts of carbon black is shown in Figure 1. Fillers give rise to similar scatter, in addition to their specific absorptions.

The more normal method[16] of treating black-loaded cured stocks is to dissolve them by refluxing with a suitable solvent (e.g., o-dichlorobenzene) followed by filtration (using a filter aid, such as Celite) to remove black; the resulting solution is vacuum concentrated and a film laid on rock salt. While the solu-
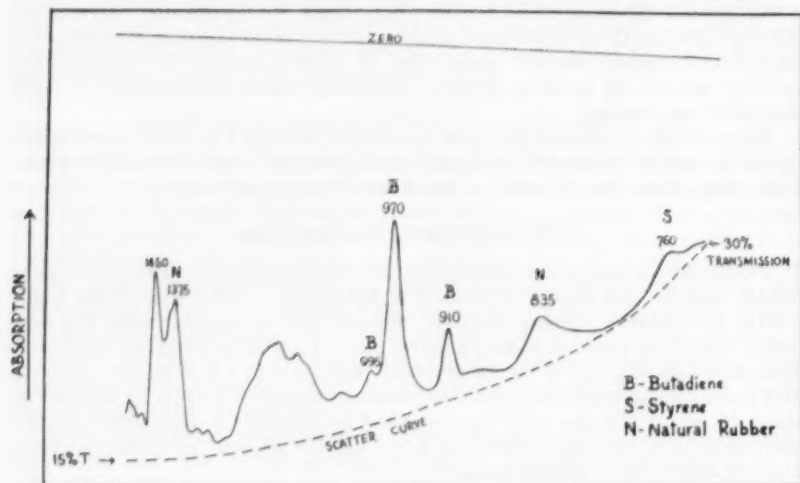
Fig. 1.—Single-beam trace of natural rubber/GR-S (66:34) mixture with 60 parts carbon black, measured with reflecting microscope.

tion method is often at present the only one available, it suffers from several serious disadvantages:

(a) excessive manipulation and refluxing time;
(b) degradation of polymers (especially apparent in the 1720 cm.$^{-1}$ region, due to oxidation);
(c) possibility of retention of polymer on filtration and consequent fractionation of mixtures.

Uncured polymers can be readily examined in several ways:

(a) In solution (not suitable for general qualitative examination).
(b) By casting films from solutions; these may be laid down on rock-salt plates or silver chloride sheets. An alternative method is to cast unsupported films on mercury or on water using rings of glass or metal to define the area and to facilitate subsequent handling.
(c) By hot-pressing or rolling. For very thin films or for elastic materials it is advisable to press between silver chloride or mica[17], the rigid sheets preventing relaxation or crumpling.
(d) In some cases, the polymer can be ground with sodium chloride[18] and then mulled with suitable liquids to reduce scatter losses.
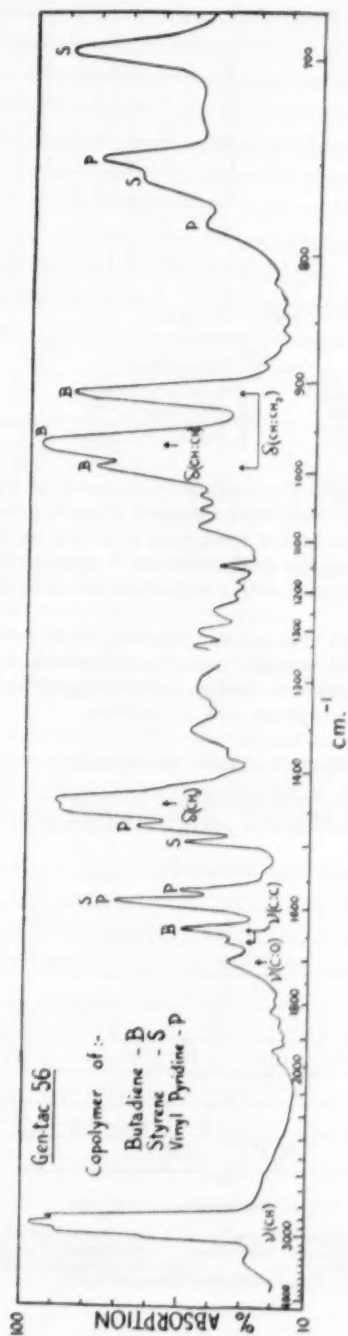
Fig. 2.—Double-beam record of Gen-tac 56 (polybutadiene/styrene/vinyl pyridine).
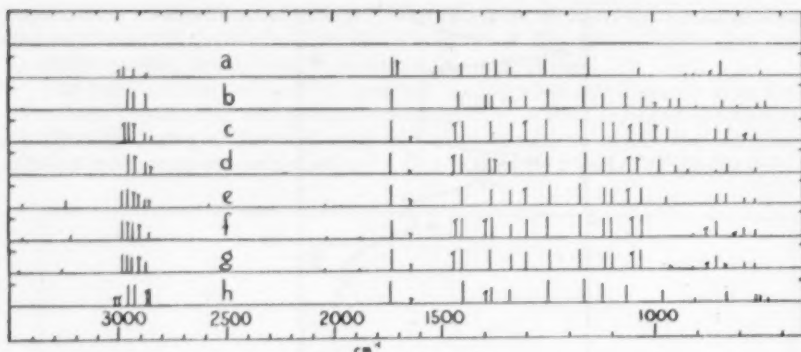
Fig. 3. Polyacrylates

a. Poly-tert-butyl acrylate.
b. Poly-n-butyl acrylate.
c. Poly-sec-butyl acrylate.
d. Poly-iso-butyl acrylate.
e. Polymethyl acrylate.
f. Polyethyl acrylate.
g. Polymethyl acrylate/ethyl acrylate; 50:50 copolymer.
h. Poly-n-hexyl acrylate.

Spectroscopic equipment.—A recording instrument of moderate resolution and speed is essential. For most work a sodium chloride prism is suitable (from 4000 to 650 cm.$^{-1}$) but the higher resolution of a lithium fluoride prism or a grating[19] is often valuable in the 4000–2000 cm.$^{-1}$ region. It is envisaged that extension of spectra to 400 cm.$^{-1}$ with a potassium bromide prism may be useful in some cases.

Unless otherwise stated, the spectra reported here were recorded with a Grubb-Parsons S.3 double-beam spectrometer, using sodium chloride and lithium fluoride prisms; the time required to record a spectrum from 4000 to 650 cm.$^{-1}$ with a sodium chloride prism was 15 minutes.

PRESENTATION OF SPECTRA

Spectra may be measured and reported in many ways. Single-beam instruments give a record of transmitted energy (I) against frequency (Figure 1),
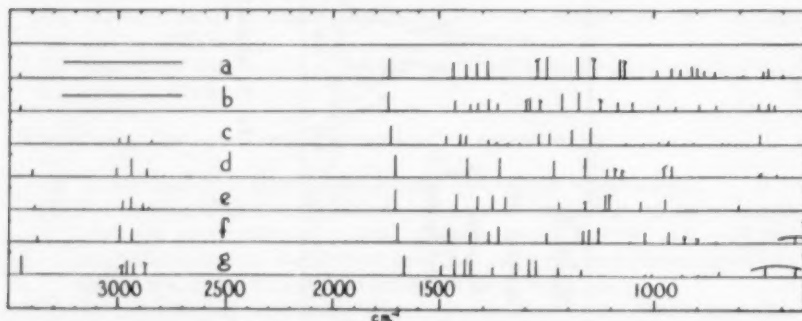
Fig. 4.—Polyesters and polyketones.

a. Polyethylene glycol adipate—crystalline.
b. Polyethylene glycol sebacate—crystalline.
c. Polymethyl methacrylate.
d. Polymethyl vinyl ketone.
e. Polyethyl vinyl ketone.
f. Polymethyl isopropenyl ketone.
g. Poly-2-vinyl pyrrolidone—hydrated.
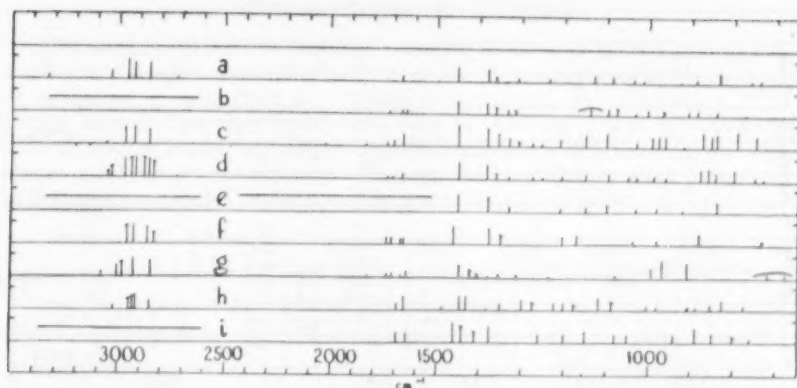
FIG. 5.—Polydienes.

a. Natural rubber.   e. Amorphous gutta.[10]
b. Synthetic polyisoprene.   f. Cyclised rubber.
c. β-Gutta.   g. Polybutadiene.
d. α-Gutta.   h. Polychloroprene.
                    i. Polydimethyl butadiene.[9]

and need comparison with a corresponding record without a sample in the beam. Double-beam instruments give direct records of percentage absorption (Figure 2) or transmission against frequency.

Frequency scales may be arbitrary ones, based upon the characteristics of a given instrument, or linear in cm.$^{-1}$ or μ. Both Figures 1 and 2 are linear with respect to the instrument calibration marks of a Grubb-Parsons S.3 spectrometer.

In comparing spectra it is often convenient to use simplified line spectra. In these, absorption maxima and shoulder are represented by lines whose height shows the percentage absorption; an indication of the contour of the band is used for shoulders or inflections and for very broad bands (Figures 3 to 8).
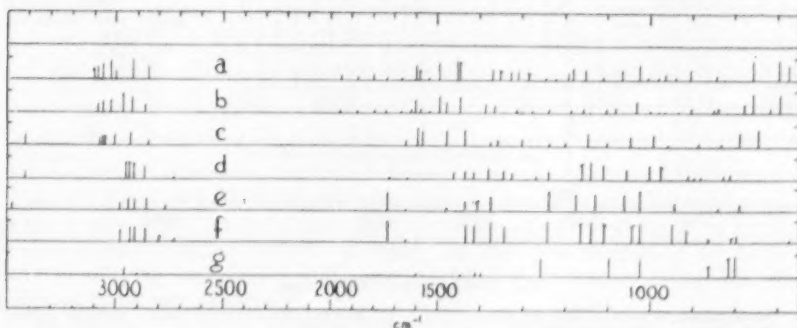
FIG. 6.

a. Polystyrene.   d. Polyvinyl butal.
b. Poly-α-methyl styrene.   e. Polyvinyl formal.
c. Poly-2-vinyl pyridine—hydrated.   f. Polyvinyl acetal.
                    g. Polymethyl siloxane—Silastic.
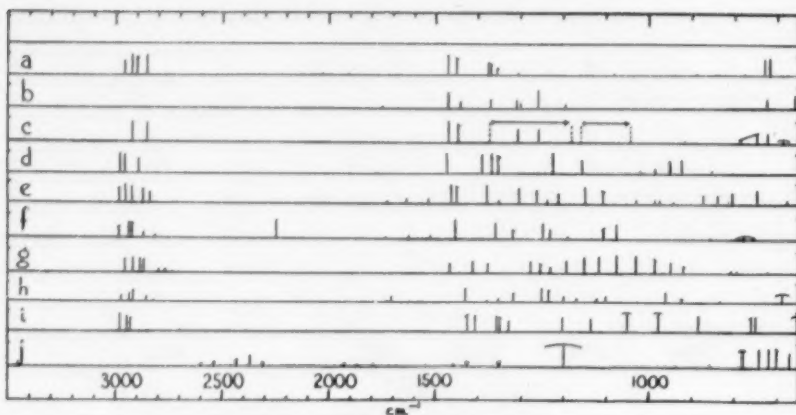
FIG. 7.

a. Polyethylene.
b. Chlorinated polyethylene (33% Cl).[5]
c. Chlorosulfonated polyethylene (Hypalon S.2).
   —arrows show shifts on curing.
d. Polyisobutene.

e. Rubber hydrochloride.
f. Polyacrylonitrile.
g. Thiokol FA.
h. Polyvinyl chloride.
i. Polyvinylidene chloride.
j. Polytetrafluorethylene.
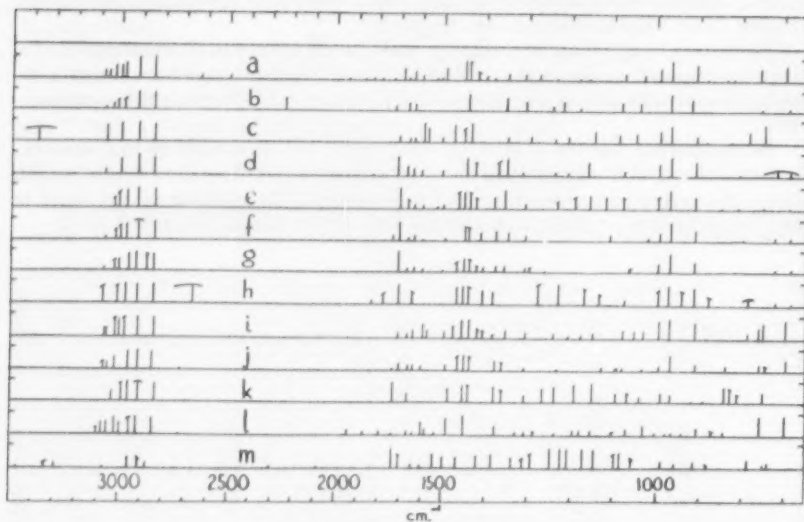
FIG. 8.—Copolymers and mixtures.

a. Polybutadiene/styrene—GR-S (75:25).
b. Polybutadiene/acrylonitrile (60:40).
c. Polybutadiene/vinyl pyridine (50:50).
d. Polybutadiene/methyl ketone (70:30).
e. Polybutadiene/methyl isopropenyl ketone
   (50:50).
f. Polybutadiene/ethyl vinyl ketone (70:30).
g. Polybutadiene/propyl vinyl ketone (70:30).
h. Polybutadiene/methacrylic acid (80:20).

i. Polybutadiene/styrene/vinyl pyridine—Gen-
   tac 56.
j. Natural rubber/GR-S (66:34).
k. Graft polymer of natural rubber and methyl
   methacrylate (80:20).
l. Polystyrene/isoprene—Isopol (75:25).
m. Polyester/urethane—German Vulkollan formed
   from polyethylene glycol adipate and
   naphthalene di-isocyanate.

INTERPRETATION OF SPECTRA

It is essential to have as complete a catalog of polymer spectra available as possible and samples from different sources should be compared to avoid basing identification or estimation on variable absorptions. For qualitative work spectra measured on other instruments may be used, but it is an advantage to have all spectra measured under comparable conditions of resolution and with similar methods of presentation. For accurate quantitative work all spectra used must be measured under identical instrument conditions.
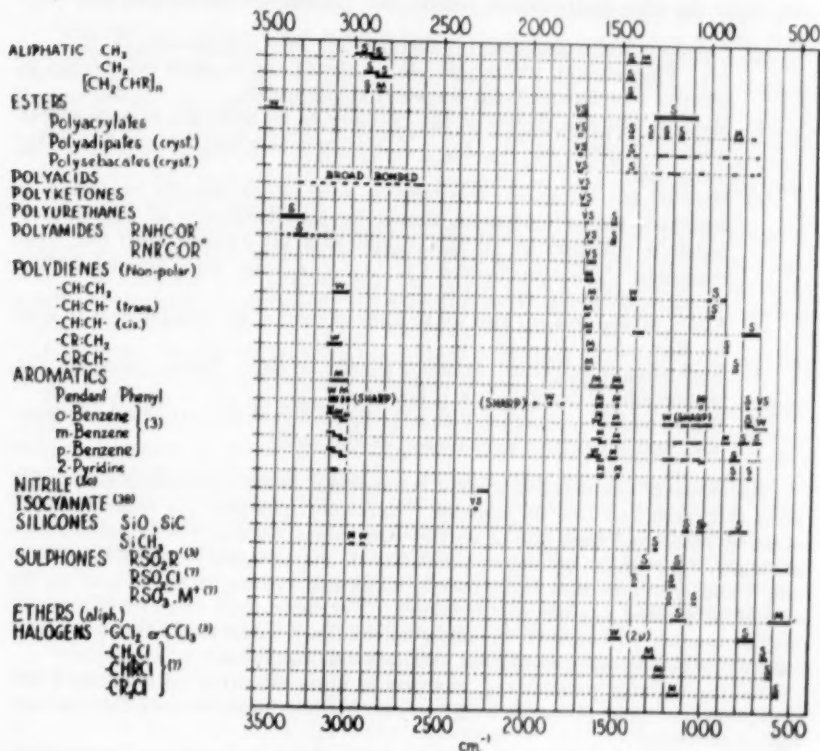
FIG. 9.—Correlation chart for polymers.

As the number of polymers available increases it will become advantageous to use a card index, either of the edge-punched hand-operated type[20] or using machine-sorted punched cards[21]. Recently, an improved method of mechanically identifying compounds and mixtures from their spectra using I.B.M. punched cards was published[22].

At present it is usual to work without such mechanical aids. From the spectrum one can classify the polymers as esters, ketones, urethanes, dienes, etc., from their functional absorptions (Figure 9). Comparison of the spectra with the line spectra (Figures 3 to 8) will generally suffice to identify most individual polymers, and direct comparison with a catalog of reference spectra

should confirm the identification, or indicate the presence of other components. Experience and a knowledge of polymer practice often narrows the search; it is advisable to check against spectra of copolymers or synthetic mixtures in the case of unfamiliar copolymers or mixtures.

QUANTITATIVE ANALYSIS

For semiquantitative analyses of mixtures it is usually possible to work from a spectrum, by direct comparison with spectra of the individual components run under the same instrumental conditions. In essence the method is:

(a) Choose suitable analytical bands for each of n components $(1, 2, 3, \cdots n)$. They should, where possible, be strong and in areas not subject to spectral interference from the other components.

(b) Measure the absorbance of the polymer to be analyzed at each of the selected frequencies $(A_1, A_2, \cdots A_n)$ using a base-line method or scatter correction.

(c) Measure the thickness; this may be done either directly (weighing or β-particle gauge[22]) or more simply by the absorbance at a frequency which is common to all the components (at 1450 or 2900 cm.$^{-1}$ for example). The absorbances $(A_1, A_2, \cdots A_n)$ are then divided by the measure of thickness used to give $S_1, S_2, \cdots S_n$.

(d) Apply procedures (b) and (c) to films of each of the components to give $R_1, R_2, \cdots R_n$.

(e) Neglecting interference, calculate $S_1/R_1, S_2/R_2, \cdots S_n/R_n$; these are the proportions of components $1, 2, \cdots n$.

(f) Where possible, compare with a synthetic mix of the estimated composition, and correct for interference as necessary.

For accurate quantitative work it is important to use films which are of uniform thickness and free of pinholes. Replicate spectroscopic measurements must be made and base line or scatter corrections measured with comparable accuracy. Instead of assuming constancy of the absorbance at 1450 or 2900 cm.$^{-1}$ and freedom from interference, analytical curves of S_1/R_1 and S_2/R_2 should be plotted against composition[16]. For more than two components it may be necessary to measure the absorbance of each component at each analytical frequency and solve a series of simultaneous equations.

Taking suitable precautions, analyses of films can often be made to 1 per cent; however, it is advisable to use solutions where possible since they permit higher accuracy.

In addition to analyses of mixtures, it is possible to determine proportions of copolymers[24,25,26] and of different structures (e.g., 1:2 and 1:4 addition in polybutadienes[24,27] and polyisoprenes[28], branching and unsaturation in polyethylenes[29,30]). In the absence of confirmation by independent methods, these require assumptions as to the constancy of the specific or molar absorptivities used; the extent to which these are justified depends upon the vibrational modes involved, and can often be judged by a knowledge of the vibrational assignments.

DISCUSSION OF INDIVIDUAL SPECTRA

Esters.—As a class these are conspicuous by the strong carbonyl stretching absorption, $\nu(C:O)$, at 1730 cm.$^{-1}$ together with bands at about 1250 and 1150

cm.$^{-1}$, $\nu\nu$(C—O—C). However, it is not always easy to distinguish between the main classes of ester polymers, i.e., (a) polyacrylates (Figure 3), (b) polymethacrylates, (c) polyesters, e.g., "Paraplex" or polyester/urethans such as Vulkollan or Chemigum SL, (d) polyvinyl esters, except by identifying the individual ester; a combination of chemical and spectroscopic methods is sometimes necessary.

Polyadipates (Figure 4a) and polysebacates (Figure 4b), either alone or in copolymers with appreciable ester regions (e.g., Vulkollans), give characteristic "crystallinity bands" in the 700 to 800 cm.$^{-1}$ region on freezing or stretching[11]. They may also be hydrolyzed and the glycols and acids examined separately.

Polymethacrylates do not readily hydrolyze under normal conditions, but their analysis by pyrolysis has been reported[21]. Pyrolysis gives good yields of the monomers, which may be identified by their spectra[21,22], although some of the copolymers give poor monomer yields on pyrolysis.

The polyacrylates give only poor yields of the monomers on vacuum pyrolysis. Polyvinyl esters on hydrolysis or ester interchange with a low boiling alcohol give polyvinyl alcohol and the corresponding acid or ester; these can be identified spectroscopically.

Ketones.—These are characterized by strong absorptions at about 1700 cm.$^{-1}$ (Figure 4). They are liable to confusion with acids, such as copolymers containing methacrylic acid (Figure 8h), but comparison of the complete spectra is sufficient to distinguish them. Among rubbers, copolymers of butadiene and vinyl or *iso*propenyl ketones may be encountered (Figure 8d to g).

Other nonelastomeric polyketones include polyvinyl pyrrolidone (which is usually hydrated[23])and copolymers of ethylene and carbon monoxide[34].

Polyurethans.—The urethan group gives strong absorptions[35,36] at ca. 3300 (νNH)), 1690 (ν(C:O)), and 1540 cm.$^{-1}$ (ν(C—N)[37]). These polymers are reaction products of di-*iso*cyanates and diols, and there is sometimes a slight *iso*cyanate absorption[38] at 2270 cm.$^{-1}$. An important new class of elastomers is the polyester/urethans which are formed by reacting di-*iso*cyanates with polyesters; their spectra show both urethane and ester bands (Figure 8m).

Polyamides.—These may be encountered as textiles or films; with some N-methyl substitution they possess elastic properties. The amides have strong characteristic bands[3,39] at about 3300, 1660, and 1540 cm.$^{-1}$. Tertiary amides, however, show only one strong band[3,37] at about 1660 cm.$^{-1}$.

Polydienes (Figure 5).—Since these give unsaturated polymers, they usually possess a ν(C=C) band at about 1650 cm.$^{-1}$. Olefinic hydrogens also give absorptions[40] at about 3000 cm.$^{-1}$, (ν(CH)) and bands in the 800 to 1000 cm.$^{-1}$ region which are dependent upon the arrangement of hydrogens about the double bond. These bands are highly characteristic in hydrocarbons[40,4] and also in a number of classes of polar compounds[32,41].

Apart from the identification of polydienes, these hydrogen deformation bands (δ(CH)) have been used for determining the proportions of 1:2 and 1:4 addition in polybutadienes[24,27,42] and in polyisoprenes[28]. The relative amounts of 1:2 and 1:4 addition may also be evidence for the method of polymerization used.

Copolymers involving butadiene (Figure 8a to j) are readily identified by the characteristic pattern of absorptions at 995, 970, and 910 cm.$^{-1}$. In the case of polybutadiene/acrylonitrile (Figure 8b), the 910 cm.$^{-1}$ band has shifted to 922 cm.$^{-1}$, and the 995 cm.$^{-1}$ is hardly observable as a weak shoulder. Comparison with vinyl and allyl cyanides[22] suggests that the repeating units are arranged

so as to give —C(CH:CH$_2$)C(CN)— groups. This is the only case of inter-action between repeating units in elastomeric copolymers observed in these laboratories, but since similar shifts occur in a number of classes of polar vinyl monomers[32], they may also occur in other copolymers of butadiene and polar vinyl compounds. Polybutadiene/vinyl ketones are however quite normal.

The sensitivity of infrared techniques to structural changes is particularly apparent in the case of polyisoprenes, since the spectra of synthetic polyisoprene, natural rubber, amorphous, α- and β-gutta percha, all show spectral differences (Figure 5a to e).

Natural rubber has a number of characteristic bands of which those at 837 cm.$^{-1}$ (δ(—CH:CMe—)) and at 1380 cm.$^{-1}$ (δ(CH$_3$)) are analytically most useful.

Polychloroprene (Figure 5h) is mainly formed by 1:4 addition and consequently has a spectrum analogous to natural rubber. Analytically significant differences are a more intense 1660 cm.$^{-1}$ band (ν(C:C)), the absence of a methyl band at 1380 cm.$^{-1}$ and a strong band at 1120 cm.$^{-1}$. The strong broad 827 cm.$^{-1}$ band is probably δ(CH:CCl) (cf. 837 cm.$^{-1}$ in natural rubber).

Little has been reported on spectra of 2, 3-disubstituted polybutadienes, apart from poly-2,3-dimethyl butadiene[5] (Figure 5i) and poly-2,3-dichlorobutadiene[6]. As a class the disubstituted polybutadienes tend to polymerize mainly by 1:4 addition, which gives only a ν(C:C) at about 1680 cm.$^{-1}$; 1:2 or 3:4 addition gives bands at about 1650 and 890 cm.$^{-1}$.

Aromatics.—Homopolymers and copolymers of styrene and its derivatives are readily identified by aromatic absorptions in the 3000 to 3100, 1600 and 1500 cm.$^{-1}$ regions, and also in the 650 to 900 cm.$^{-1}$ and 950 to 1250 cm.$^{-1}$ regions depending upon the substitution patterns[3,4].

Pendant monosubstituted benzene rings as in polystyrene (Figure 6a), and GR-S (Figure 1, 8a), have a large number of characteristic bands which make their identification very easy. Although no ring-substituted polystyrenes have been examined in this laboratory, it is anticipated that they would be equally distinctive.

Polyester/urethans from aromatic di-*iso*cyanates (Figure 8m) also have aromatic bands at 3100, 1600 and 1500 cm.$^{-1}$ but differ in other regions.

Polymers of 2-vinylpyridine also have aromatic bands at 3000 to 3100 and 1590 cm.$^{-1}$ which are similar to those of styrene, but differ in possessing bands at 1573, 1477, 790, 748 cm.$^{-1}$ (Figures 2, 6c, 8c, and 8i).

Nitriles.—The nitrile group gives a sharp absorption band at 2240 cm.$^{-1}$ which is quite distinctive and has been used for quantitative analysis[16]. Where the spectrum shows urethan groups, there may be a weak band at 2270 cm.$^{-1}$ due to residual *iso*cyanate[38]; however, these frequencies can just be distinguished with a sodium chloride prism and readily so with a lithium fluoride prism.

Sulfones.—Hypalon S.2, which is a polyethylene with chlorine and chlorosulfonyl substituents[7] is most readily distinguished from polyethylene and halogenated polyethylene[6] by absorptions at 1158 cm.$^{-1}$ and 1370 cm.$^{-1}$ (due to the chlorosulfonyl group) in the uncured state. These bands shift to 1160 and 1060 cm.$^{-1}$ (ionic sulfonate) on vulcanization (see Figures 7a to c). No vinyl sulfone polymers have been examined, but RSO$_2$R groups should give rise to strong bands[3] at 1290 to 1350 and 1100 to 1170 cm.$^{-1}$.

Silicones.—As in the case of lower molecular weight silicones[43], the silicone rubbers (Figure 6g) are characterized by strong bands at 1025 and 1090 cm.$^{-1}$ (arising from the Si-O skeleton), a strong sharp band at 1257 cm.$^{-1}$ which has

been assigned to the Si-Me group, and strong bands near 800 cm.$^{-1}$ which are assigned to $\nu\nu(\text{Si—C})$. As would be expected the $\nu(\text{CH})$ region for polymethyl siloxanes is unusually simple, consisting of only two bands ($\nu_a(\text{CH}_3)$ and ν_s-(CH_3)).

Silica, which may be encountered as a reinforcing agent, also has a strong absorption at 1100, with a shoulder at about 1180 cm.$^{-1}$, and a medium absorption at 800 cm.$^{-1}$.

Polyacetals.—These are characterized by the $\nu\nu(\text{COC})$ absorptions at ca. 1135 cm.$^{-1}$. Samples usually contain residual acetoxyl and hydroxyl groups, the former being indicated by the $\nu(\text{C=O})$ at 1733 cm.$^{-1}$ and the latter by an absorption at about 3450 cm.$^{-1}$. For identification of the individual polymers, a direct comparison with the spectra of known polyacetals is required (Figures 6d to f).

Miscellaneous polymers.—Thiokol FA has a quite distinctive spectrum (Figure 7g), but little work has been reported on other thioplasts. Dinsmore and Smith[16] comment that the bands in the 1100 cm.$^{-1}$ region are probably due to ether groups, but that the S—S and C—S—S—C bands cannot be assigned. It would be expected that these latter groups would give weak bands[6,44] at about 600 ($\nu(\text{C—S})$) and 500 cm.$^{-1}$ ($\nu(\text{S—S})$); these would require a potassium bromide prism.

Butyl rubber is readily identified by bands at 1226, 948, 920 cm.$^{-1}$, and a doublet (due to C(Me)$_2$ groups) at 1389, 1365 cm.$^{-1}$. It is not distinguishable from polyisobutene (Figure 7d).

Hydrogenated polybutadiene[45] has a very similar spectrum to polyethylene (Figure 7a), differing mainly in showing residual unsaturation and branching. Polyethylene is also variable in these respects[30,29], and without further work on these compounds it would be unwise to attempt to differentiate them spectroscopically in samples of unknown origin.

Polyethylene itself, though not an elastomer, is used for electric cables and may also be blended with polyisobutene. In such cases, it can usually be identified by the doublet at 725 cm.$^{-1}$ which becomes a single band on melting. Since this depends upon crystallization[29], it would not be suitable for estimating the polyethylene content.

Polyvinyl chloride (Figure 7h) is readily identified by a band at 1430 cm.$^{-1}$ ($\delta(\text{CH}_2)$ lowered by chlorine) and bands at 1250 and 960 cm.$^{-1}$. It is often met copolymerized with vinylidene chloride, the repeating units of which have strong bands at 1050 and 1410 cm.$^{-1}$ (Figure 7i).

Fluorine polymers such as polyperfluoro acrylates and polyfluoroprene are elastomers which may have application for special purposes. They should show strong $\nu(\text{CF})$ bands in the 1000 to 1350 cm.$^{-1}$ region[2] in addition to the other functional groups. The line spectrum of polytetrafluorethylene is given for interest (Figure 7j), and demonstrates the absence of hydrogen (no bands near 3000 cm.$^{-1}$) and the presence of fluorine by strong bands at about 1200 cm.$^{-1}$ ($\nu(\text{CF})$) and overtones at about 2350 cm.$^{-1}$ ($2\ \nu(\text{CF})$).

Although not elastomers, rubber derivatives are of interest in the industry, and spectra of a number have been reported[46]. Cyclized rubber, which may be used in blends with natural rubber, is readily identified by a strong band at 880 cm.$^{-1}$ (Figure 5f). Chlorinated rubber also shows this absorption, which has been variously assigned to RR'C:CH$_2$[46] and a cyclohexyl ring[47]; the latter appears more plausible.

LIMITATIONS AND FUTURE DEVELOPMENTS IN
INFRARED ANALYSIS

In the last few years the complexity of problems submitted has increased rapidly and a few cases have already arisen in which a purely infrared examination has been inconclusive. This indicates the importance of developing supplementary techniques for the analysis of elastomers and polymers generally.

Improvements in spectroscopic technique will help considerably. These include microspectroscopy, both for examination of smaller samples and for black-loaded stocks; extension of the spectral range below 650 cm.$^{-1}$, and improved resolution in the 4000 to 2000 cm.$^{-1}$ region. Polarized radiation is sometimes useful with oriented samples[48]. Improved methods of sample preparation and of film thickness measurement are equally important.

However, in some cases spectral differences are insufficient to permit estimation or even differentiation, and supplementary techniques are required. It is often possible to use chemical methods, physical properties, ultraviolet spectroscopy, x-ray examination[49], and even considerations of technical practice, availability, and economics. However, it would be convenient to be able to use auxiliary techniques available within the spectroscopic laboratory. Combinations of chemical and spectroscopic methods have already been used, e.g., pyrolysis[1,31], hydrolysis of polyesters[11], and bromination of polyethylenes[30].

Although infrared spectroscopy often permits analyses of polymers for which no practical alternative methods exist, the problem is so complex that no single technique can be expected to meet every case.

SUMMARY

Infrared absorption spectroscopy is the most generally applicable technique available for the analysis of elastomers and other polymers encountered in the rubber industry. The emphasis of this paper is on the general identification and estimation of a wide range of elastomers, rather than the accurate quantitative analysis of particular copolymers and mixtures.

The theoretical basis of spectra, particularly of polymers, is described. The additivity of absorbances is the basis of quantitative analyses, for which the procedures are outlined. Although theoretically some interaction between repeating units is to be expected, most repeating units have the same spectra whether in homopolymers or copolymers.

Experimental techniques are described for preparing samples for spectroscopic examination from both uncured and cured materials. The latter, particularly when reinforced with carbon black, often give difficulty since they transmit insufficient energy for direct examination. As an alternative to solution or pyrolysis, a reflecting microscope may be used to increase the amount of energy available for measurement of the spectrum.

Spectra of a large number of homopolymers, copolymers, and mixtures are reported from 650 to 3600 cm.$^{-1}$, mostly in simplified line form. Polymers covered include polydienes, polyvinyl and isopropenyl compounds (including polyketones and acrylates), polyesters, polyurethans, modified polyethylenes, and silicones.

A summary of absorptions characteristic of particular polymer structures is given in the form of a correlation chart.

The limitations of the technique are discussed, and probable future developments are suggested, i.e., extension of the spectral range below 650 cm.$^{-1}$,

improved techniques of sample preparation, and combinations of spectroscopy with chemical procedures such as pyrolysis.

ACKNOWLEDGMENTS

CONFERENCE DISCUSSION

Dr. Gordon congratulated the authors on being the first, as far as he was aware to show an infrared spectrum on a highly black-loaded specimen. That was of very great importance and it would be interesting if more details could be given of the microscope mentioned by Mr. Davison which achieved that result.

With regard to the infrared method in general it was very difficult to distinguish between rubber and ebonite, although fortunately he was able to distinguish between them by other methods.

Mr. Davison, in reply, said that the final point was not literally correct; the spectrum of rubber was significantly different from that of ebonite. However, it was only slightly modified by soft vulcanization[6]; this was largely due to the weak absorption of bands involving sulfur.

It was an advantage of the technique for polymer identification that it was relatively independent of the state of cure, molecular weight, and other complications.

The use of the microscope was simple in principle, although it had not been used before for this purpose. Using a numerical aperture of about 0.65, much more of the scattered energy was collected than with a normal spectrometer (numerical aperture of about 0.1). Preliminary measurements showed that the percentage of energy transmitted using the reflecting microscope was about 20 times that which was transmitted with a normal spectrometer.

Dr. Bethell, referring to Figure 1, in which there appeared the scatter curve, asked whether the authors had ever placed any quantitative reliance on that, and measured the intensitites of various components, or did it vary so much from one type of loading to another that no quantitative reliance could be placed upon it?

Mr. Davison stated that the scatter curve should be related to the size of the carbon black aggregates. However, since the main emphasis of this work was on identification they were unable to assess the quantitative accuracy of work with highly scattering systems.

Under conditions of severe scatter, one would expect a distribution of spectral path lengths which would somewhat distort intensities and reduce the accuracy of quantitative analyses.

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EVALUATION OF RUBBER TO METAL BONDS *

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INTRODUCTION

The art of bonding rubber to other materials, such as textiles, wood, leather, and metals is long established and the first use of rubber adhesives can be traced to the period when vulcanization of rubber with sulfur was discovered. Progress in the art of bonding did not keep pace with developments in the field of vulcanization and although the industry developed many successful techniques for bonding rubber to metal these techniques all had disadvantages which prevented the expansion of rubber bonded units into the wide field of engineering uses known today. Up to 1939, when the first effective proprietary chemical bonding agents were marketed, the bonding methods favored by industry were the ebonite technique, protein-latex systems, cyclized rubber based adhesives, and the technique involving the brass plating of the metal. The ebonite method is still in use today for selected applications, where its shortcomings are of little consequence. Brass plating continues to be used by those companies who already have the necessary equipment even though it suffers from many drawbacks. The criticisms levelled against it are that it involves considerable capital expenditure, the cleaning of the metal units must be carefully supervised and the composition of the brass deposited must be vigilantly controlled. Unless the brass surface is immediately protected by a suitable film surface oxidation results, causing a decrease in adhesion. Many of the materials used in this process are toxic and care has to be taken in disposing of the effluents.

The difficulties of controlling the brass-plating technique are well known and during the 1939–45 war these difficulties were discussed at length and in detail by industry and the Services Committee. Brass plating was not considered suitable for bonding to light alloys and this was a severe limitation as many applications required the manufacture of units based on synthetic rubbers and aluminum or Duralumin. As late as 1945 many reports stated that the normal brass plated bond with natural rubber was of the order of 500 lb. per in.^{2} and one problem put to Imperial Chemical Industries Ltd. was "to confirm that claimed bond strengths of 900 to 1000 lb. are obtainable" with brass plating. It is significant that at this time several organizations reported that they seldom were able to classify their broken test pieces as "break in the rubber". The importance of developing bonding systems which would withstand fatigue was realized as it was claimed "that fatigue had been known to cause 80 per cent failures in the case of certain units". The above statements illustrate that ten years ago the bonding of rubber to metal for engineering uses was at a stage when many factors concerned with the process were still shrouded in mystery. Even those companies with established reputations for their ability in producing rubber to metal units will probably agree that much greater progress has been achieved in the last ten years than in the remainder of this century. A

wider range of metals and rubbers have been employed successfully; considerable improvements have been made in the design of units; appreciable reduction in the number of rejects has provided industry with welcome proof that bonding to metal can be done reproducibly and economically.

The efficiency of chemical systems for rubber/metal bonding has improved steadily over the last decade; partly due to the improvement of the chemical agents themselves but also due to their wider use leading to greater experience and the development of improved bonding techniques.   The following factors, for example, are known to be important:

   (1) Selection of the best method of cleaning the metal surface, e.g., abrasion, shot or sand blasting, acid etching and degreasing.
   (2) Careful selection of the stock used in preparing the interply solution and also of the solvent or solvent mixture.
   (3) Drying conditions of the bonding agent and the interply solution.

It is easy to demonstrate by simple tensile tests when the rubber/metal bond is either very poor or very good.   In the first case the bonded unit will separate completely at the bonded interface under very low applied load.   In the second case high breaking loads are obtained.   In the great majority of cases showing moderate to good bonding the rubber/metal interface is almost always affected to varying degrees in a manner which is fortuitously related to the actual breaking load.   The appearance of the broken unit is of little value as a criterion in judging the efficiency of the bonding system.

Many attempts have been made in the past[1,2] to discriminate clearly, by a suitable choice of testing method, between different rubber/metal bonding systems.   This distinction becomes increasingly difficult as the rubber/metal bond is improved and if the strength of the rubber stock is reached any differences in the bond strength that may remain cannot be revealed.   Furthermore, it is most important in comparative work of this nature that a good rubber to metal bond should first be reproducibly obtained; otherwise subsequent test results merely reveal a very large variability reflecting poor technique in the fabrication of the bond itself.

The object of the present paper is to review recent work on the evaluation of rubber to metal bonding systems using testpieces fabricated by both compression and transfer molding and tested by a variety of methods.   Every effort has been made, by the control testing of a large number of testpieces, to ensure uniformity of the bonding process and the variability of the test results is indicated where appropriate.

The three systems investigated are those based on:

   (1) A chemical derivative of rubber (CDR) to mild steel.
   (2) A polyisocyanate (PI) to mild steel.
   (3) Solid brass of the following composition:

Copper	70.5%	Tin	Nil
Lead	0.01%	Iron	0.01%
	Zinc	29.48%	

It should be noted that the rubber bond has been made directly to brass and not to brass-plated testpieces.   As will be shown in the paper the plating process can often detract seriously from the usefulness of the rubber to brass bond, and it was desired to make the comparison with the chemical systems free from this bias.

EXPERIMENTAL DETAILS

The following high-resilience stock, typical of those widely used in rubber to metal bonding applications in the industry, was selected for all the present work. This stock had the following composition and physical properties:

Smoked sheet	100	Lamp black	30
Zinc oxide	5	Sulfur	3.5
Stearic acid	3.5	Mercaptobenzothiazole	1
Liquid cumar gum	2.5	Antiflexcracking antioxidant	1

Four mm. sheets of this stock press cured 28 minutes at 141° C had the following properties:

Tensile strength	3000 lb./in.^{2}
Modulus at 100%	274 lb./in.^{2}
300%	930 lb./in.^{2}
500%	2060 lb./in.^{2}
Elongation at break	665%
Hardness	62 B.S.°
Resilience at 22° C	74%
Resilience at 50° C	76%
Tear strength at 22° C	670 lb./in.^{2}
Tear strength at 50° C	650 lb./in.^{2}

TESTPIECES AND TESTING METHODS

ASTM testpieces.—These were made according to ASTM Designation: D.429-47T but with the thickness of the rubber reduced to $\frac{1}{4}$ inch. All references to ASTM testpieces in the text are to discs of this size and thickness.

The above testpieces were used in the following testing methods:

Tensile break.—Testpieces were stretched to break in a Denison machine at a jaw separation of 1 inch per minute. The breaking load in pounds was registered.

Compression fatigue.—A Goodrich Flexometer, modified to accommodate the testpieces, was used for this method. The speed of flexing was 1430 r.p.m. No static load was applied, the compression stroke increasing from zero to 0.05 inch (20 per cent compression) and returning to zero in one flexing cycle.

Impact test.—The testpieces were subject to impact loading in extension using the falling weight impact machine previously described[1,2]. However, some modifications in the use of this method were adopted as follows:

(1) The impact of the falling weight with the striker plate is inelastic, i.e., the falling weight and striker plate remain in contact after initial impact and therefore move with a common velocity in deforming the rubber testpiece. The loss of kinetic energy on impact is calculable in terms of the mass of the falling weight and the mass of the striker plate, and must be allowed for by adjusting the height from which the weight falls. It can be shown that

$$L = \frac{I(M + m)}{M^2}$$

where L = height of fall (ft.) of weight M (lb.)

m = mass (lb.) of striker plate

I = energy input (ft. lb.) to testpiece.

This formula has been used throughout for calculating the height of fall required to give impacts of known energy input.
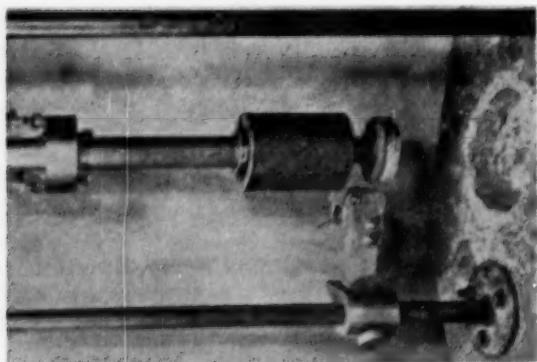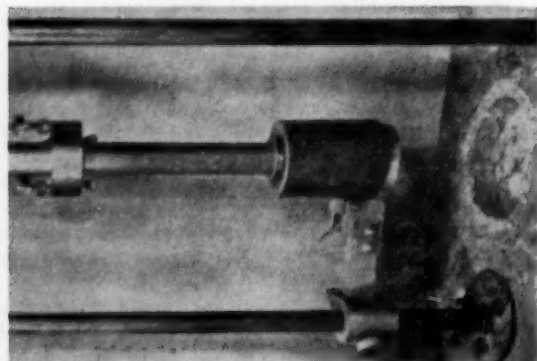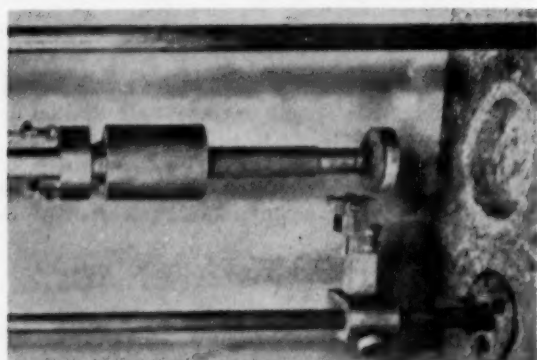
Fig. 1.

(2) With the original design of the impact test[1,2] the elasticity of the test-piece results in a diminishing succession of rebound impacts of the falling weight. The loads[3] imposed on the testpiece by these rebound impacts are not always negligible in relation to the first impact loading. A simple mechanical switch was therefore designed by means of which the falling weight is arrested after the first rebound: testpieces therefore receive only one impact of known energy input (referred to as a single arrested impact). Figure 1 (a, b, c) shows the sequence of operations of this device.
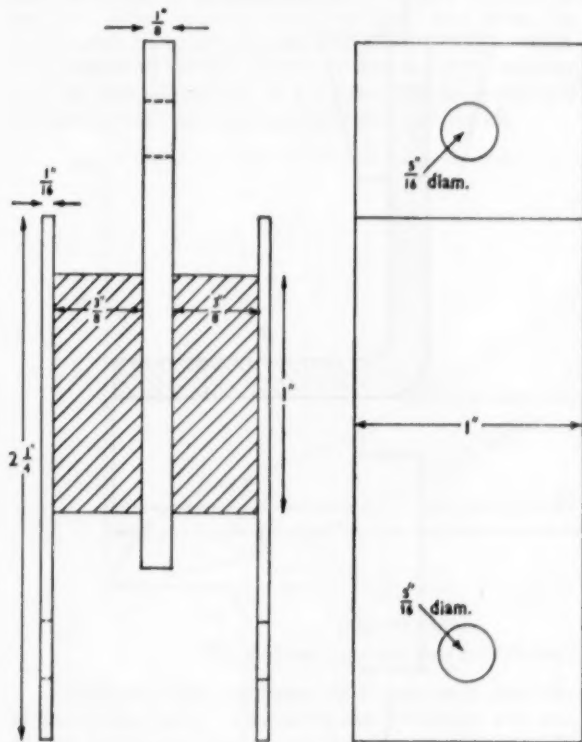
FIG. 2(a).—Shear test-piece.   FIG. 2(b).

Shear testpieces.—Figure 2 (a) shows a dimensioned sketch of the double-sandwich type of shear testpiece used; Figure 2 (b) shows a testpiece stretched in the Denison machine.

The above testpieces were used in the following test methods:

(a) *Tensile break.*—Testpieces were stretched to break in a Denison machine at a jaw separation of 1 inch per minute. The breaking load in pounds was registered.

(b) *Dynamic shear fatigue.*—No suitable machine was available in which the test-pieces could be subjected to high-speed dynamic shear of large amplitude. The following severe slow-speed test was therefore adopted. The test-

piece was strained to 1800 pound load in the Denison machine at 4 inches per minute jaw separation, followed by retraction to zero load. This cycle of operations was successively repeated at a rate of 1.33 cycles per minute. The number of complete cycles before break was recorded.

90° peeling test.—A version of this test, originally developed by the Lord Manufacturing Company and now being considered as a revision of ASTM D.429-47T, was used. Figure 3 shows a dimensioned sketch of the testpiece.
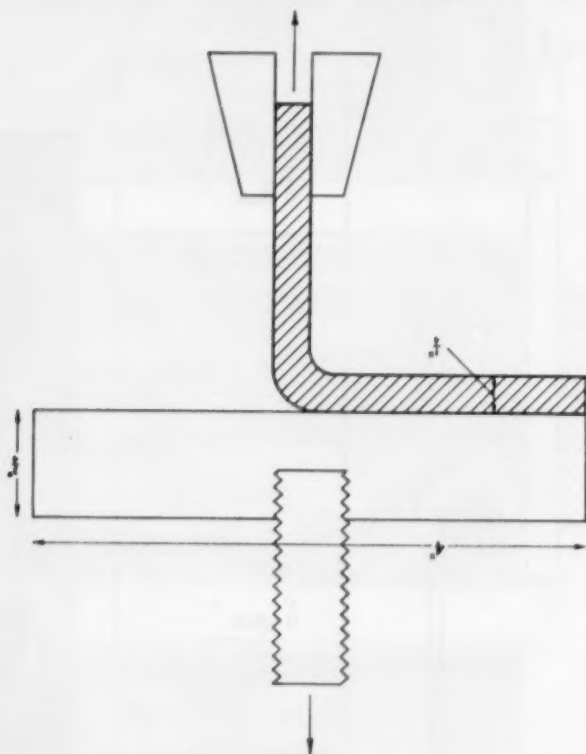
FIG. 3.—90° peeling test-piece.

The 2-inch wide bonded rubber of thickness 1 inch was stripped to within ½ inch of the center; peeling over an inch length was then carried out in the Denison machine at a jaw separation of 4 inches per minute. The variation of peeling load in pounds up to the final steady value was recorded.

BONDING CONDITIONS

Brass.—The brass units were cleaned by abrading on emery cloth. They were then immediately immersed in dry trichlorethylene; this acted as a degreasing bath and as a barrier to oxidation. After removal from the bath, as the last traces of trichlorethylene were evaporating, an interply solution was

applied by brush. This solution consisted of 20 parts of the stock described dissolved in 80 parts of toluene. After air drying for 60 minutes at ambient laboratory temperature, the units were bonded to the rubber stock during the curing process.

In the case of the brass-plated units described, these were plated industrially, coated with the cement described above shortly after plating and bonded a few days later.

CDR system.—The units were cleaned by abrading on emery cloth and were then immersed in trichlorethylene to remove traces of grease and other foreign matter. After removal from the bath and when the trichlorethylene had evaporated, one uniform coat of a CDR cement, which had been well stirred, was applied by brush. After air drying for 60 minutes, the interply solution used for the preparation of the brass testpieces was applied and air dried for 60 minutes and the bonding operation completed.
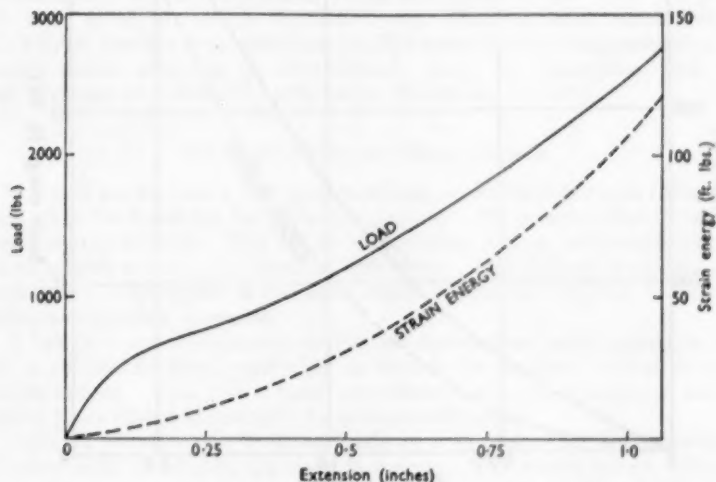
Fig. 4.—Load-extension curve of A.S.T.M. test piece.

PI system.—The mild steel units were steel shot blasted prior to immersion in trichlorethylene. Thereafter the procedure was as described for the CDR system except that the interply solution was based on Pool Rubber Solvent and not toluene, since toluene is an excellent solvent for the PI film and causes it to lift from the metal surface and admix with the interply layer.

Molding details.—The ASTM test specimens prepared by compression molding were all cured in hot molds in a direct steam heated autoclave using a curing cycle of 28 minutes at 40 lb. steam pressure and a molding pressure of 330 lb. per in².

The transfer molded units and the peeling samples were press cured using the same curing cycle and a molding pressure of 1500 lb. per in².

BASIC DATA

Figure 4 shows the tensile load-deflection curve of an ASTM disc together with the corresponding strain energy curve, when tested on the Denison at a

rate of travel of the lower jaw of 1 inch per minute. It should be remembered that in extension this type of test-piece suffers considerable constriction or necking.

Owing to the complicated stress distribution with an ASTM sandwich in extension all the test results in straight pull on ASTM discs have been expressed simply as the breaking load in pounds; any attempt to reduce these to breaking stresses at the bonded interface is thought to be quite unrealistic.

Figure 5 shows the load-deflection curve of a shear testpiece and the corresponding strain-energy curve when tested at a rate of travel of the lower jaw
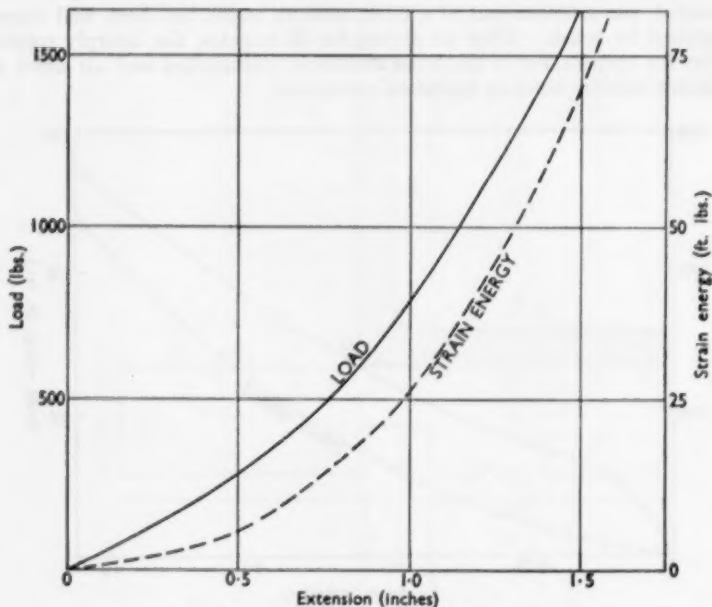
FIG. 5.—Load deflection curve of shear testpiece.

of 1 inch per minute. It will be seen that the deformation is by no means "pure shear" and the test results have again been expressed as the breaking load in pounds rather than in shear stress at break.

EXPERIMENTAL RESULTS AND DISCUSSION

THE APPEARANCE OF THE BROKEN UNIT: AN INDIFFERENT CRITERION

Table I shows the tensile breaking loads of two sets of rubber to brass bonded ASTM units. One set represents moderately good bonding; the other, poor set, was purposely obtained by modification of the fabrication technique. The "type" of break is simply assessed by giving the proportion of the brass visible at the bonded surfaces after tensile break.

It is seen from Table I that only when the bonds are bad, resulting in 100 per cent interface failure, does the appearance of the bonded surface after break give any indication of the quality of the bond. When the bond obtained is

TABLE I

Poor		Moderately good	
Breaking load lbs.	% Brass visible lbs.	Breaking load lbs.	% Brass visible lbs.
560	100	2270	40
380	100	2130	10
400	100	2310	90
450	100	1920	10
500	100	2000	45
470	100	2000	80

moderately good the appearance of the broken bond bears no relation at all to the load required to break it. This applies to all bonding systems. When chemical systems, involving the use of tie-solutions, are employed the appearance of the broken surfaces is even more complicated and confusing. It is for this reason that a complicated visual assessment of the "type" of break, such as is given in ASTM D.429-47T, and which is being considered by ISO/TC/45, has not been attempted in this paper and it is suggested that this practice should generally be discontinued. Only the "all-rubber" and "all-bond" failures are intelligibly reflected in the broken surfaces.

THE VARIABILITY OF BRASS–PLATING

It is well known that a very good bond can be obtained between rubber and brass, when the brass has the right composition. We consider that 70 copper: 30 zinc is very suitable. The use of brass plating, e.g., on mild steel, does not give so reliable a bond as is obtained with brass. It is difficult to say precisely to what this unreliability is due since many factors are involved in both the plating and bonding processes.

It has been our experience over the last decade that brass plating on mild steel is subject to great variability as regards its use as a rubber to metal bonding system. This view is based on tests carried out on a very large number of units brass plated industrially by several companies.

Table II shows tensile breaking loads on a number of ASTM brass-plated mild steel units, bonded by the same technique. The results for six testpieces prepared on three separate occasions are given in columns I, II and III.

It is thus seen that bond strengths ranging from good to bad can be obtained with brass plating using the same bonding technique and rubber compound. The above results are typical of those to be expected with the brass-plate system and render it unsuitable as a criterion of comparison for other bonding systems.

Table III shows a comparison of bonds between rubber to brass and rubber

TABLE II

TENSILE BREAKING LOADS ON BRASS-PLATED UNITS IN POUNDS

I	II	III
2000	1000	520
2100	1500	500
2560	870	410
2280	1300	600
2500	840	590
2000	1000	610
2240	1090	540

TABLE III

DYNAMIC COMPRESSION FATIGUE OF BRASS BONDING SYSTEM

Number of cycles (million)	0	0.171	0.513	1.37
Brass bond	2470 lb.	2380 lb.	2380 lb.	2160 lb.
Brass-plate bond	2690 lb.	1870 lb.	1260 lb.	920 lb.

to brass-plated mild steel for ASTM units subjected to a dynamic compression of 20 per cent at 1430 r.p.m. and tested for tensile break after varying periods of fatiguing.

It is significant that the results quoted in Tables II and III were accompanied by a variety of types of fracture as follows:

(1) Limited failure at rubber to brass interface.
(2) Almost complete failure between brass plate and mild steel.
(3) Splitting of brass plate film.
(4) Almost complete failure at rubber to brass-plate interface.

It will be seen from Table III that although a good bond (as judged by tensile break) was initially obtained with the brass-plated units the dynamic fatigue test reveals a marked deterioration compared with the solid brass bond.

Consideration of Tables II and III clearly justifies our decision to use the brass bond as a criterion in preference to the brass plated bond.

COMPARATIVE TEST RESULTS ON THE THREE SYSTEMS

Tensile breaks at 1 inch per minute.—Table IV shows the results obtained for the three bonding systems investigated. The figures quoted are each based on 12 testpieces and show (1) the mean value of breaking load in pounds, (2) the standard deviation (pounds) and (3) the coefficient of variation (per cent) of the individual test results.

The following conclusions can be drawn from Table IV:

(1) With the ASTM bonded discs there is no significant difference between the three bonding systems either with compression or transfer molded testpieces. The overall mean figure for tensile load to break (mean of 72 testpieces) is 2500 pounds, with a standard deviation of 247 pounds and a coefficient of variation of 10 per cent. This degree of variability, approaching that obtained in the tensile testing of rubber stocks, can be considered satisfactory for bond fabrication and testing.

TABLE IV

TENSILE BREAKING LOADS IN POUNDS

Type of molding Type of testpiece	Compression ASTM	Transfer	
		ASTM	Shear
CDR 1	2510	2340	2360
2	203	260	270
3	8%	11%	11%
PI 1	2680	2470	2540
2	194	292	359
3	7%	12%	14%
Brass 1	2470	2540	2820
2	292	305	147
3	12%	12%	5%

It is interesting to note that ASTM D.429-47T suggests that the normal variation to be expected in this test is ±100 pounds on the mean of two results. However, the magnitude of the average value is not specified. On this basis it is possible to have a wide range of variability depending upon the level of bond strength achieved. In the event of the two results not conforming to the above, D.429-47T permits the simple averaging of five results. The present data suggests that the variability of this test can be properly and more usefully expressed as the coefficient of variation of the test results.

(2) In all cases some rupture of the bonded interface was visible in the broken testpiece but the appearance and amount of this visible failure was extremely variable and bore no relation whatsoever to the individual breaking loads of the testpieces.

(3) With the shear testpieces (fabricated by transfer molding only) there is no significant difference between the mean breaking loads of the chemical bonding systems but the brass bond gives a significantly higher breaking load. In view of the general uniformity of results with the ASTM testpieces two possibilities suggest themselves:

(a) The shear test discriminates more effectively between bond strengths than the ASTM method or

(b) the fabrication of the shear testpieces has introduced another factor not present in the molding operations of the ASTM test discs.

It is not easy to decide on present evidence between these two views but the following fact may be relevant. The transfer mold used in making the shear testpieces had eight injection ports all of which were almost flush with the metal surfaces to be bonded. A mold design of this type may be satisfactory for brass bonding but should not be used in bonding operations employing chemical bonding agents. In our opinion the differences between the bonding systems furnished by the shear results in Table IV represent the relative susceptibility of the bonding systems to "wiping" by the injected rubber stock rather than inherent differences in the rubber to metal bond obtained.

Further comments on these shear testpieces are given later under *Dynamic tests*.

Impact tests.—Table V shows the results obtained by subjecting the ASTM testpieces to repeated shock loading in elongation on the falling weight impact machine. The test conditions were identical in all cases, viz., a 20-pound weight falling freely through 4.0 feet, corresponding to an actual energy input to the testpiece of 70 foot pounds. Rebound impacts were arrested and the number of single blows required to break the testpiece was determined. The figures quoted refer to six testpieces and show (1) the mean value, (2) the standard deviation and (3) the coefficient of variation of the individual results.

The following conclusions can be drawn from Table V:

(1) With the exception of the PI system in compression molding the variability of the test results is much greater than that of the tensile break results given in Table IV. A larger number of testpieces would be required to obtain a confident estimate of the true variability. From this experiment it is not possible to decide whether the variability given in Table V is due to the test method or is a real reflection of variability of the bonding as revealed by this test.

TABLE V

MULTIPLE IMPACTS AT 70 FT. LB. ENERGY

Molding process Testpiece		Compression ASTM	Transfer ASTM
CDR	1	11.2	21.5
	2	3.3	5.3
	3	30%	25%
PI	1	10.0	22.0
	2	0.8	8.6
	3	8%	39%
Brass	1	10.5	13.0
	2	2.6	4.3
	3	25%	33%

(2) There is no significant difference between the average values of the three systems in compression molding or between the brass system in either compression or transfer molding. The CDR and PI systems in transfer molding, however, are both significantly higher than the other mean values, although no such difference was revealed in the tensile break test.

In view of the similarity of results, both in mean value and variability, between the CDR and brass systems in compression molding these two systems were examined in greater detail over a range of impact energy levels (Table VI). In addition, the tensile load to break was also measured after impact fatigue at each energy level (Table VII).

A number of interesting points arise from Tables VI and VII. (1) There is excellent agreement between the average number of blows to break for the two systems in the lower energy levels from 50 to 100 ft. lb. (Table VI). It was found that all the testpieces at the 50 ft. lb. level had broken completely in the rubber, the only occasion on which all-rubber breaks were observed with ASTM testpieces. It follows, therefore, that about 30 blows of low (50 ft. lb.) energy input are sufficient to fatigue and break the rubber stock. At the 70 and 97 ft. lb. levels traces of bond rupture were visible in the broken testpieces; hence it is likely, under these conditions, that bond strength determines the break.

(2) At the higher energy input levels (above 120 ft. lb.) the testpieces show a persistent "refusal" to break consistently in one blow. It is possible that at these high energy levels the supports of the present machine begin to bend and interpose an energy-absorbing spring in series with the testpieces (cf. Appendix II, Reference 1).

TABLE VI

IMPACT TESTS AT DIFFERENT ENERGY LEVELS

ASTM Compression Molded Testpieces

Impact conditions				Average no. of blows to break	
Mass of weight (lb.)	Height of fall		Energy input to testpiece ft. lb.		
	ft.	in.		CDR	Brass
20	2	10	50	29.8	30.5
20	4	0	70	11.2	10.5
20	5	6	97	6.0	6.0
30	4	4	120	5.3	3.0
30	4	9	130	3.0	2.0
30	5	5	150	2.7	2.0

TABLE VII

TENSILE BREAK FOLLOWING IMPACT FATIGUE AT DIFFERENT ENERGY LEVELS

ASTM Compression Molded Testpieces

Mass of weight (lb.)	Height of fall ft.	Height of fall in.	Energy input to test-piece ft. lb.	No. of impacts given	CRD	Brass
20	2	10	50	20	2090	1980
20	4	0	70	6	2000	1970
20	5	6	97	3	2460	2170
30	4	4	120	2	2210	2320
30	4	9	130	1	2600	2840
30	5	5	150	—	—	—

(3) At the two lowest energy levels of 50 and 70 ft. lb. the testpieces, after pre-treatment by impact (Table VII) subsequently show a uniform level of tensile load to break. This is lower than the overall average figure of 2500 lb. given by the unimpacted testpieces and in view of (1) above probably represents fatiguing of the rubber stock by impact. At the higher energy levels of impact (above 70 ft. lb.) the higher tensile loads indicate that fatigue of the bond or the rubber has not occurred under the small number of impacts given.

On the above results little or no difference can be distinguished between the CDR and brass bonding systems. The results do, however, emphasize the difficulties of unequivocally separating the effects of fatigue of the rubber stock from failure of the bonding interface at low or moderate impact energies. They support previous suggestions that impact tests for bond strength would best be carried out by the "Probit" method[1,2,4] in which the energy level is found that will just consistently break the unit in a single blow.

With the high levels of bond strength attainable with the systems discussed here it should be remembered that care must be taken to ensure that the supports of the impact machine are sufficiently rigid as high impact energies are required to break testpieces of these dimensions in a single blow. This difficulty can be reduced by using thinner testpieces and this may yet be necessary if the bond strength is raised to higher levels by further improvements in bonding agents and techniques.

Dynamic tests.—(1) *ASTM testpieces on Goodrich Flexometer.* ASTM discs, fabricated by compression molding, were flexed on a Goodrich Flexometer at 1430 r.p.m. under a compression stroke of 20 per cent. No static load was applied. After 2, 6 and 16 hours' flexing the testpieces were broken in straight pull and the tensile breaking load measured. Table VIII summarizes the results:

Table VIII shows that there is little or no difference between the bonding systems under compression fatigue. At 1.37 million cycles the tensile breaking load is still 81–89 per cent of its initial value. With all the testpieces break-

TABLE VIII

DYNAMIC COMPRESSION FATIGUE

No. of cycles compression (million)	0 lb.	0.171 lb.	0.513 lb.	1.37 lb.
CDR	2510	2430	2120	2040
PI	2680	2550	2400	2390
Brass	2470	2380	2380	2160
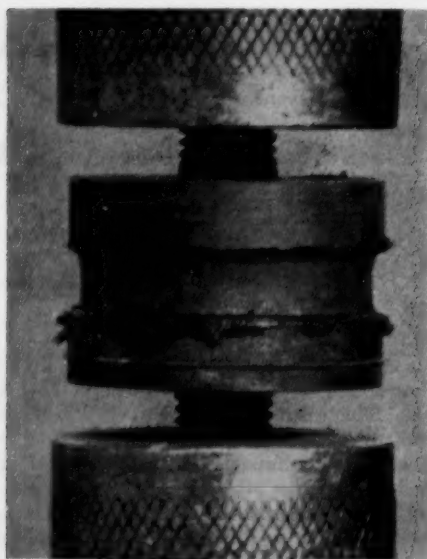
FIG. 6.

down of the rubber stock near the edges of the metal discs began after about 0.1 million cycles; after 1.37 million cycles a narrow fringe of degraded stock was present in all testpieces. This effect is shown in Figure 6, the fatigued testpiece having been photographed under very slight extension. It is probable that fatigue of the rubber stock is the major factor in determining the breaking load. However, it is extremely difficult to separate this fatigue from any fatigue of the bonded interface proper.

Although dynamic fatigue in extension is not a normal service type test, a comparison between the CDR and brass systems was made under these conditions where flexing was carried out at 1430 r.p.m. with an extension amplitude of 0 to 42 per cent. The tensile breaking loads after different periods of fatiguing are given in Table IX.

Table IX shows that in both cases the progressive loss of tensile breaking load is virtually the same, the testpieces losing 50 per cent of their initial breaking load after about 24 minutes' flexing, i.e., after 34,300 cycles of extension. In all cases degradation of the rubber had begun around the edges of the discs and the increasing degradation of the body of the rubber stock was clearly visible in the broken test-pieces.

(2) *Shear testpieces.*—With the shear testpieces high-speed flexing of small amplitude produced negligible breakdown of the unit over very long periods.

TABLE IX

DYNAMIC FATIGUE IN EXTENSION

No. of cycles extension (thousand)	0 lb.	7.15 lb.	14.3 lb.	28.6 lb.	57.3 lb.
CDR	2510	1930	1860	1450	540
Brass	2470	2050	1700	1320	820

A slower but more severe test was therefore used in which a load of 1800 pounds was applied and released in a cycle of 45 seconds' duration (1.33 c.p.m.) This load is equivalent to approximately 400 per cent shear strain. The number of complete cycles which the unit withstood before breaking was recorded. The results (average of 6 testpieces) are given in Table X:

TABLE X

DYNAMIC SHEAR FATIGUE

	No. of cycles before break	Coefficient of variation
CDR	11	23%
PI	7	30%
Brass	7	27%

In all cases in this test, where actual rupture of the unit occurs under the dynamic load, the visual appearance of the individual broken shear units could not be related to their flex life. In Table X there is no difference between the PI and brass systems but the CDR system is superior.

It will be recalled from Table IV that the CDR system was inferior to brass in simple tensile break. It thus appears that the simple tensile test may not be a reliable guide to the dynamic behavior of the bonding system when the dynamic loads imposed are less than the tensile breaking load.

90° peeling test.—The testpieces were made by compression molding and the load measured to peel the rubber at 90° to the metal. The speed of jaw separa-

TABLE XI

90° PEELING TEST

Bonding system		Load to peel (lb./in. width)	Type of break
CDR	(a)	120–165	All-rubber
	(b)	100–150	All-rubber
	(c)	110–170	All-rubber
PI	(a)	110–150	All-rubber
	(b)	120–190	All-rubber
	(c)	100–145	All-rubber
Brass plate	(a)	85–100	70% rubber, 30% metal
	(b)	95–115	98% rubber, 2% metal particles
	(c)	75–85	60% rubber, 40% metal patches

tion was 4 inches per minute. Not sufficient metal was readily available to make the brass testplates of solid brass; mild-steel units were therefore brass-plated industrially for this test. Table XI gives the individual results obtained together with the type of break observed.

In Table XI the first figure quoted refers to the load at which peeling started; thereafter the load increased in a series of steps up to the final steady value given by the second figure. These average steady peeling values for the three test-pieces are:

CDR	160 lb. per in. width
PI	160 lb. per in. width
Brass plating	100 lb. per in. width

It is obvious that with the chemical systems the loads imposed on the bonded interface are insufficient to break it; in these cases the load to peel is limited by

the tear strength of the rubber stock. The reduced value with brass plating and the appearance of the peeled units are another example of the difficulties encountered with this system.

In a peeling test of this nature it may be useful to classify the type of break as is recommended by the ASTM and ISO/TC/45. As stated earlier in this paper we recommend rejection of the method of classification for straight pull, impacts and fatigue tests, but we prefer to reserve final judgment and to continue using such classifications with peeling tests for the time being, until further evidence is collected.

CONCLUSIONS AND SUMMARY

During the last ten years improvements in bonding agents and their technique of application have enabled industry to manufacture with greater surety a wider range of rubber to metal components. This welcome advance continues but as the level of bond strength is raised certain problems associated with testing become more acute. It has always been a simple matter to differentiate between poor and good bonding. However, considerable thought and care in testing and interpretation are required to differentiate between good bonding agents and techniques when the bond strength is high. Industry is faced with two types of testing problem; control of factory production and evaluation of improved techniques (including different bonding agents). The question of control of factory production is not dealt with in this paper although some of our conclusions could usefully be applied in the field of control testing.

Examining each of the test methods employed in the present paper it may be useful to summarize the salient features that appear to us to have some importance.

It is axiomatic that the strength of a rubber to metal bond can not be assessed without breaking the adhesion between the rubber and the metal. However, only in the case of poor adhesion, where separation occurs entirely at or within the bonded interface, are breakdown tests easily and unequivocally related to the bond strength. When good bonds of high breaking strength are obtained it becomes a matter of great difficulty to discriminate between different bonding systems.

The simple straight pull test has been employed for many years in spite of the obvious criticisms that can and have been levelled at it. There is no doubt that simple measurements of tensile breaking load give a clear indication of whether or not a good bond has initially been obtained in the molding process. From Table IV it is deduced that the variability of this test should not exceed that given by a coefficient of variation of about 8 to 12 per cent of the mean value; values greater than this indicate that more careful control of the bonding process is required.

Interesting results are reported with testpieces tested in shear; on a tensile break test the brass bond appeared superior to both CDR and PI bonding agents but this superiority was not retained in the dynamic test where the CDR was better than either the brass or PI bond.

A simple mechanical switch has been fitted to the impact machine to ensure that the falling weight is arrested after the first rebound. With transfer molded testpieces the CDR and PI systems are more resistant to multiple impacts than the brass bond. At low energy inputs (50 ft. lb.) the rubber stock appears to fatigue before the bond but at inputs of 70 ft. lb. and above it is believed that fatigue of the bond occurs. This observation is important as the data obtained

under a variety of dynamic conditions in this paper emphasize the difficulty of discriminating clearly between the fatigue of the rubber and fatigue of the bond. Since different dynamic tests, e.g., impact and shear flexing, discriminate differently between bonding agents, classified as equally good by simple tensile break tests, it is clear that in laboratory comparisons of bonding systems a variety of tests is essential.

Using a 90° peeling test, the chemical bonding agents could not be distinguished since all-rubber breaks occurred. The brass-plated bond however, failed at a lower level of peeling load with evidence of bond rupture.

There is no doubt that very good bonds can be consistently obtained to 70/30 brass. Brass plating, however, is a much more variable system and is quite unsuitable as a standard of comparison in laboratory work. The CDR and PI systems are capable of giving results at least equal to those obtainable with solid brass, and one would hesitate to claim any clear superiority of one over the others.

The process of obtaining a good bond between rubber and metal is not one which is easy to reproduce without careful control of the rubber stock, the interply solution, the metal surfaces, the bonding agent and the molding technique. This applies to all bonding systems at present known to us.

Except in cases of very poor adhesion the appearance of the broken unit is indifferently related to the bond strength and cannot be used as a criterion in assessing bonding systems or bond strength.

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